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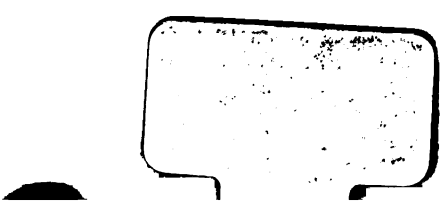

FIRST

PRINCIPLES

OF

MODERN CHEMISTRY.

A Manual of Inorganic Chemistry

FOR STUDENTS AND FOR USE IN SCHOOLS AND SCIENCE CLASSES.

BY

U. J. KAY-SHUTTLEWORTH, M.P.

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PREFACE

TO THE FIRST EDITION.

WHILST this little book is an attempt to supply the want of a strictly elementary manual of inorganic chemistry, adapted for use in science classes, I have also endeavoured to indicate how, with the aid of modern theories, a student's early steps may be made less tedious and more suggestive than they commonly are.

Dr. Frankland, with a kindness for which I cannot thank him sufficiently warmly, has assisted me by most valuable advice, as well as by revising the whole of the manuscript and proofs.

The lectures delivered by Dr. Williamson at University College, in the Session 1864–5, and those of Dr. Frankland at the Royal College of Chemistry, in the following winter, supplied me with a considerable part of the matter here collected together.

I have also gratefully to acknowledge the readiness with which Professor Tyndall has sanctioned the use I have ventured to make of his treatise on "Heat con-

sidered as a Mode of Motion;" whilst to the authors of the books enumerated below I owe many apologies for the extent to which I have availed myself of their statements or explanations of facts:—Dr. William Allen Miller's "Elements of Chemistry," Parts i and ii; Dr. Frankland's "Lecture Notes for Chemical Students;" Professor Roscoe's "Lessons in Elementary Chemistry;" Professor Naquet's "Principes de Chimie;" Dr. Atkinson's Translation of Professor Ganot's Elementary Treatise on Physics.

For the study of the Metals and their compounds the reader is referred to more complete works, as the time and space at my command have kept the present volume almost within the limits to which the examination in chemistry is restricted at Matriculation in the University of London. Nor have detailed directions as to manipulation and apparatus been attempted: indeed such directions are seldom very intelligible except when given orally in presence of the objects used; and it may be assumed that practical study in a laboratory should always accompany a course of reading on chemistry.

Old methods for the description of chemical changes are retained in the following pages; for the atomic theory and its more modern adjuncts—though founded only in part on experimental data, and sure ere long to pass away—have a temporary value which it would be short-sighted to overlook.

I have employed the system of notation proposed by Dr. Frankland, in the belief that its advantages ought

to insure its almost universal adoption. As I have also made use of Dr. Crum Brown's graphic formulæ, it may be as well—once and for all—to protest against the imputation that those who use graphic formulæ are liable to fall into the error of regarding them as pictures of the physical arrangement of atoms. This objection to a method which teachers have found of great value, in bringing home to their pupils' minds essential ideas on the constitution of compounds, is not supported by the experience of many who have given it an impartial trial.

Since I have found it difficult to avoid the use of several terms which seldom occur in books of general reading, I have added a short glossary giving the meanings and derivations of such of them as have escaped a full explanation in the text.

In conclusion, I would assure any of my readers who may find mistakes to correct, or improvements to suggest, how grateful I shall feel if they will communicate with me without delay.

GAWTHORPE HALL, BURNLEY,
December, 1867.

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FIRST PRINCIPLES

OF

MODERN CHEMISTRY.

Chapter I.

INTRODUCTORY CONSIDERATIONS.

Chemistry, like other natural sciences, treats of matter.

Matter may be defined to be that which has *weight* or is *ponderable.* Matter is continually undergoing changes of various kinds, and these changes are produced by

Forces.—Amongst the forces to which such changes are due, may be reckoned heat, electricity, gravity, cohesion, chemical affinity, or the chemical force, &c. Each force acts according to fixed laws, which it is the first function of the sciences to discover and investigate. The study of such forces as heat, electricity, gravity, cohesion, &c., is called Physics; whilst the science of Chemistry, which treats especially of the composition of bodies, is the study of the chemical force, and of the laws which govern its action.

Chemical Affinity.—We shall best understand what is meant by chemical affinity, or the chemical force, if we proceed to determine how it differs and how it may be distinguished from other forces.

i. The exertion of the chemical force between different forms of matter is always accompanied by a marked change in the properties of the kinds of matter on which it acts.

For example, the gas oxygen produces, with the hard

greyish-white metal iron, the brown friable oxide of iron which we call rust; acting on heated magnesium wire, oxygen sets up a brilliant combustion and produces the white bulky infusible compound called magnesia, of which the white smoke of a magnesium lamp consists. By the chemical combination of the gases hydrogen and oxygen water is formed; whilst the mere contact of the invisible gases hydrochloric acid and ammonia is sufficient to cause their conversion into the white solid, sal-ammoniac.

ii. The chemical force is unable to exert any action between substances which are not in absolute contact; in other words, it cannot bring about any change when the substances between which it is to act are separated by an appreciable space; and here it differs from all other forces, except cohesion and adhesion.

Through the ninety-one millions of miles which separate us from the sun, solar light and heat reach us; gravity and other forces also produce their effects through distances equally vast. The perfection of the contact required, on the other hand, for the exertion of chemical affinity is exemplified by such facts as the following :—Clean bright iron may be left for any length of time in dry air or oxygen without the formation of a particle of rust; but, if the air be damp, so that moisture in which the oxygen of the air may become dissolved is deposited on the surface of the iron, the oxygen and iron are brought into sufficiently complete contact to enable oxidation to commence, and rust appears. When placed in apparent contact, solids which are not volatile do not act chemically on each other. No action, for instance, takes place in a mixture of iron filings with flowers of sulphur; though, if proper means be taken for bringing the iron and sulphur into absolute contact, a great amount of chemical affinity is manifested between them. A more familiar example of this fact is afforded by gunpowder,—a mixture of charcoal, sulphur, and nitre, finely powdered, and most intimately mixed by grinding and pressure. The contact thus brought about, though apparently

absolute, is not so perfect as to set up the chemical action of which these constituent substances are capable. But they may be brought into such contact by the application of heat; and, consequently, gunpowder when heated is converted into gas and smoke. Some solids *appear*, at first sight, able to act chemically on each other; *e.g.*, a violent action takes place when the solids iodine and phosphorus are brought together; but the fact is that both substances are volatile, and that the commencement of the action takes place between their vapours.

iii. The chemical force is always exerted between fixed and invariable quantities of matter.

For example, hydrogen and oxygen never combine except in fixed proportions by weight and by volume. Thus two pounds of hydrogen require sixteen pounds of oxygen with which to combine; and a cubic foot of hydrogen requires for combination half a cubic foot of oxygen. If less oxygen be supplied to the hydrogen, some of the latter is left uncombined; but the proportion by weight of oxygen in the compound formed, namely water, is still always as 16 to 2, and the proportion by volume as 1 to 2.

Recapitulating these distinguishing characteristics of the chemical force, we may say, that when chemical affinity is manifested between two or more different kinds of matter they must be in perfect and absolute contact; that it causes in them a marked change of their original properties; and, lastly, that it always exerts itself between fixed and invariable proportions of the different kinds of matter.

When it is said that under the action of chemical affinity the properties of substances disappear and alter, it must not be forgotten that chemical affinity, like heat and other forces, is quite unable to alter one property of substances, namely, their weight, or the action of the force of gravity upon them: *e.g.*, 16 lbs. of oxygen combining with 2 lbs. of hydrogen, give 18 lbs. of water. For conversion into rust, 7 lbs. of iron need exactly 3 lbs. of oxygen, and the oxide produced

weighs 10 lbs. And in no process of chemical action, in no combustion, for example, does any loss of weight take place. There is no such thing as destruction or loss of matter; nor can the chemical force cause any change in the action of the force of gravity upon matter, however much the form and properties of this matter may be altered.

FORMS OF MATTER.—We have already had to speak of different forms or kinds of matter. Of these there are on the earth an infinite number. For our purposes we shall have to distinguish between two or three classes of forms of matter, namely, (i) "elements" and mixtures of elements, and (ii) "compounds."

i. *Elements.* An element may be defined to be a kind of matter out of which it has been impossible to obtain any different kind of matter, or a body which has resisted all attempts to resolve it into simpler forms of matter. It is a *simple* or *indecomposable* body.* The revelations of chemical discovery have shown how comparatively small is the number of elements entering into the composition of the innumerable forms of matter around us. At present the number of supposed elements does not exceed sixty-two, and of these a large proportion—about one-third—may be called "chemical rarities."

ii. *Compounds* are substances which consist of two or more different elements, held together by the force of chemical affinity.

A substance may contain several elements and yet not be a compound, because the elements are not held together by the chemical force; such a substance is a *mechanical mixture.* We have observed how complete are the changes in properties accompanying chemical action. Mere mechanical mixture produces no change in properties; for the constituent parts of a mixture always retain their original properties

* This definition is founded on Dalton's principle "that a substance, till it is decomposed, must be regarded, according to the just logic of chemistry, as an elementary substance."

without any alteration, and, since they are not held together by chemical affinity, are capable of being separated with much greater ease than bodies which have combined to form a chemical compound. These facts may be illustrated by numerous examples :—A *mixture* of a cubic foot of hydrogen with half a cubic foot of oxygen is a transparent, colourless gas, which explodes violently when ignited. The explosion or *combination* results in the production of a few drops of water. A *mixture* of iron filings with flowers of sulphur is readily resolved into its original elements by mere physical means. This may be done very effectually by sifting, still better by a magnet, which removes the iron, and perfectly by a certain liquid (carbonic disulphide or bisulphide of carbon), which dissolves out all the sulphur, leaving all the iron. But the *compound* of iron with sulphur is not attracted by the magnet; nor can sulphur be abstracted from it by means of any solvent. Mixtures of compounds, and mixtures of elements with one or more compounds, differ in the same manner from compounds; they can be resolved into their constituent parts by mere physical means. For instance, from gunpowder, which we have already stated to be a *mixture* of the elements carbon and sulphur with the compound nitre, water will dissolve out the nitre, and carbonic disulphide the sulphur, whilst the carbon remains. But the gases resulting from the combustion of gunpowder, when the chemical attractions between these substances have been brought into play, cannot yield up their constituents to any such agents.

Systematic Chemistry.—It is then under the influence of the chemical force that the comparatively few known elements arrange themselves into the numberless compounds which constitute so vast a proportion of the different forms of matter around us. To study the chemical force, and to investigate and discover the laws which govern its action is, as we have said, the primary object of the science of chemistry; it is obviously indispensable to the attainment of this object first to examine the elementary bodies and their simpler compounds,

and then to extend our investigations to more complex substances, applying to them the considerations to which the study of the more rudimentary portion of our subject has introduced us. With a view to this systematic treatment of the several parts of chemistry, it is convenient to make a broad distinction between what may be called the two great provinces of the science, namely:—

i. *Inorganic or Mineral Chemistry*, which treats of inorganic substances, or of the elements and of such of their compounds as may be obtained from the mineral kingdom.

ii. *Organic Chemistry*, which treats of organic substances, or compounds which may be obtained from the vegetable and animal kingdoms.

Between these provinces it is neither necessary nor possible to draw any clear boundary line, since chemists have succeeded in obtaining a great number of organic substances —a number to which almost daily additions are being made— from the mineral kingdom. In this volume, however, we shall confine our attention to the province of inorganic chemistry, and shall find it unnecessary either to enter upon the study of more than a small portion of this province, or to say much about any substances which have ever been regarded as purely organic.

Atomic and Molecular Weights.—Since the chemical force is exerted between *fixed and definite quantities or proportions* of the different forms of matter, it is convenient to adopt hydrogen, which combines with other elements in a smaller proportion by weight than any other body, as the *unit* of "combining proportions," or "proportional numbers," that is, to represent its combining proportion by the number 1, and to fix that of every other element according to this standard. The elements combine with one another only in the ratios expressed by these numbers, or by multiples of them; this is called the law of *definite and multiple proportions*. To these numbers, expressing the combining proportions of the elements, the name "atomic weights" has also been given,

because those ultimate particles of matter between which the atomic theory of Dalton supposed the chemical force to be exerted, according to the law of definite and multiple proportions, were called *atoms*. For instance, chlorine and hydrogen are two elements; they combine to form hydrochloric acid; 1 lb. of hydrogen unites with $35\frac{1}{2}$ lbs. of chlorine, and 1 atom of hydrogen is said to unite with 1 atom of chlorine; hence, the combining proportion of hydrogen being unity, that of chlorine is 35·5, and the weights of these imaginary atoms are to each other as 1 to 35·5; if what we agree to call the atomic weight of hydrogen be taken as unity, that of chlorine is, therefore, 35·5.

Further, when elements enter into combination, their atoms are said to combine to form *molecules;* thus an atom of hydrogen uniting with an atom of chlorine is said to form a molecule of hydrochloric acid; and the "molecular weight" of hydrochloric acid is 36·5, or the sum of the atomic weights of its component atoms. An atom of hydrogen may also combine with a second atom of hydrogen, to produce a molecule of hydrogen; hence the molecular weight of hydrogen is 2.

We may thus define the terms *atom* and *molecule*, in the sense to which they will here be carefully restricted. The *atom* (ἄτομος, indivisible) of an element is the smallest particle thereof which is capable of existing in *chemical combination.* The *molecule* (= little mass, dimin. of *moles*, a mass), of an element or compound, is the smallest quantity capable of existing in the *free or uncombined state.*

Symbols.—For convenience' sake symbols are used to denote the atoms of elements. Thus, for an atom of hydrogen the letter H is used, for the atom of chlorine the symbol Cl, of oxygen O, &c.; and the molecule of hydrochloric acid is represented by the symbol HCl,—for it is customary to denote combination by the apposition of symbols. A small figure placed after a symbol, thus H_2, expresses the number of

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for the most part denizens of matter and do not readily conduct heat or electricity well. The distinction is neither exact nor philosophical, though for some purposes it is convenient.

The next two chapters are devoted to some of those elements of physics which it is indispensable that the student should thoroughly understand before he attempts to enter upon the consideration of the more special part of our subject. The study of HEAT occupies a large share of these chapters. The importance of mastering as completely as possible the accounts of common phenomena given under that head can scarcely be overrated. If the reader has any difficulty in perceiving the drift or following the examination of anything that is said upon heat, he is recommended to consult Professor Tyndall's work on "Heat considered as a Mode of Motion," to which frequent reference will be made, and from which—with Professor Tyndall's permission—the author has condensed a large part of the few following pages on the elements of physics.

Students who are preparing for the Matriculation Examination of the University of London will find that the subject of heat is here treated very much in the order laid down in the University Calendar, and that the knowledge of heat required in that examination is not more than they can gather from these chapters.

atoms employed; a number placed before a symbol or formula indicates the number of molecules, as $2H_2$, — 3HCl.

It cannot be too emphatically impressed upon the student that the symbols do not stand for indefinite proportions and quantities of the elements, but that they represent fixed and definite proportions. The equation—

$$H + Cl = HCl$$

does not mean that any quantity of hydrogen and any quantity of chlorine, added together, enter into combination and form so much hydrochloric acid. What is meant is, that when any quantity of hydrogen unites with 35·5 times its weight of chlorine the result is a quantity of hydrochloric acid the weight of which is 36·5 times as great as that of the hydrogen employed.

THE ELEMENTS.—These introductory pages, the contents of which the beginner must not expect thoroughly to understand at once, will receive ample illustration before we have proceeded far in the study of the elements. A list of these will be found at the end of the present chapter, with their symbols and atomic weights. The atomic weights of those elements whose names are printed in capital letters should be committed to memory by degrees. They are the only elements to which we shall pay special attention; with a few exceptions, they belong to the class of elements ordinarily called "Non-metallic." The remaining elements, with one or two doubtful exceptions, usually receive the name of "Metals;" it is highly desirable that the student should remember the atomic weights of some of the more important of these also; but he need spend no time in learning either the names or the atomic weights of those elements whose names are printed in the smallest type; as most of them are of rare occurrence, and, so far as we yet know, of the smallest practical importance.

The metals are, as a rule, lustrous bodies, and good conductors of heat and electricity; the non-metallic elements are

for the most part destitute of lustre, and do not usually conduct heat or electricity well. The distinction is neither sharp nor philosophical, though for some purposes it is convenient.

The next two chapters are devoted to some of those elements of physics which it is indispensable that the student should thoroughly understand before he attempts to enter upon the consideration of the more special part of our subject. The study of HEAT occupies a large share of these chapters. The importance of mastering, as completely as possible, the accounts of common phenomena given under that head can scarcely be overrated. If the reader has any difficulty in perceiving the drift or following the explanation of anything that is said upon heat, he is recommended to consult Professor Tyndall's work on "Heat considered as a Mode of Motion," to which frequent reference will be made, and from which—with Professor Tyndall's permission—the author has condensed a large part of the few following pages on the elements of physics.

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TABLE OF THE ELEMENTS.

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
ALUMINIUM	Al	27·5	Molybdenum	Mo	92
ANTIMONY (Stibium)	Sb	122	NICKEL	Ni	58·8
ARSENIC	As	75	Niobium	Nb	97·6
BARIUM	Ba	137	NITROGEN	N	14
BISMUTH	Bi	208	Osmium	Os	199
BORON	B	11	OXYGEN	O	16
BROMINE	Br	80	Palladium	Pd	106·5
Cadmium	Cd	112	PHOSPHORUS	P	31
Cæsium	Cs	133	PLATINUM	Pt	197·12
CALCIUM	Ca	40	POTASSIUM (Kalium)	K	39·1
CARBON	C	12	Rhodium	Ro	104
Cerium	Ce	92	Rubidium	Rb	85
CHLORINE	Cl	35·5	Ruthenium	Ru	104
CHROMIUM	Cr	52·5	SELENIUM	Se	79
COBALT	Co	58·8	SILICON	Si	28·5
COPPER (Cuprum)	Cu	63·5	SILVER (Argentum)	Ag	108
Didymium	Di	96	SODIUM (Natrium)	Na	23
FLUORINE	F	19	STRONTIUM	Sr	87·5
Glucinum	Gl	14	SULPHUR	S	32
GOLD (Aurum)	Au	196·7	Tantalum	Ta	137·5
HYDROGEN	H	1	TELLURIUM	Te	129
Indium	In	74	Thallium	Tl	204
IODINE	I	127	Thorium	Th	231·5
Iridium	Ir	197·12	TIN (Stannum)	Sn	118
IRON (Ferrum)	Fe	56	TITANIUM	Ti	50
Lanthanum	La	92	Tungsten (Wolframium)	W	184
LEAD (Plumbum)	Pb	207	Uranium	U	120
Lithium	Li	7	Vanadium	V	137
MAGNESIUM	Mg	24	Yttrium	Y	64
MANGANESE	Mn	55	ZINC	Zn	65
MERCURY (ὑδράργυρος)	Hg	200	Zirconium	Zr	89·6

Chapter II.

WEIGHTS AND MEASURES, SPECIFIC GRAVITY, AND HEAT.

Physical Conditions of Matter.—Matter may exist in three distinct physical conditions, that is, either in the *solid*, the *liquid*, or the *gaseous*, *aeriform*, or *vaporous* state. Ice, water, and steam (or aqueous vapour) are examples of these three conditions.

In *solid* bodies the molecules are so held together by cohesion that they are not capable of much motion upon each other.

In *liquids*, though the force of cohesion still resists the separation of the molecules, they have full liberty of motion amongst each other.

In the *vaporous* or *gaseous* condition the molecules are freed from the influence of cohesion.

Just as we have observed that the chemical force has no power of altering the weight of substances, so we must here remark that the degree in which cohesion does or does not exert its power in a substance cannot in the least degree affect its weight. An ounce of ice yields, on melting, an ounce of water, which, by the aid of heat, may be converted into an ounce of steam.

Weights and Measures.—Before we proceed further, it is necessary that we should adopt some system with the aid of which we may express and readily compare different quantities of matter—that is to say, some plan which will enable us to state clearly, first, the relative dimensions of, and, secondly, the relative effects of gravity upon, different sub-

stances,—and, thirdly, their "specific gravities," or the relations between their bulks and weights.

English physicists and chemists have found our old-fashioned systems of weights and measures so cumbersome and inconvenient, and they have deemed it so important that they should use the same weights and measures which are used by scientific men on the continent, that, for the most part, they have adopted the French metrical system. The beautiful simplicity and harmony of this system will be readily recognised by the student, who will find a few minutes' study amply sufficient to acquaint him with all its details. He will also soon discover how very great is the amount of time and trouble in calculation which he will save by making himself thoroughly conversant with its use. On these accounts, and further because a knowledge of the metrical weights and measures is expected by Examiners in Physics and Chemistry, they will be adopted throughout this volume. A sketch of the system, sufficient for the student's purposes, is, therefore, given at the outset:—

The Metrical System.

Linear Measures.

Unit – 1 *metre* = $\frac{1}{40000000}$th of the *meridian* (or the circumference including the axis) *of our planet.*

	Metres.
Millimetre =	0·001 or $\frac{1}{1000}$th of a metre.
Centimetre =	0·01 or $\frac{1}{100}$th ,,
Decimetre =	0·1 or $\frac{1}{10}$th ,,
Metre =	1
Decametre =	10
Hectometre =	100
Kilometre =	1,000

Cubic Measures.

Unit — 1 *cubic metre.*

		Cub. Metres.
Cubic millimetre	=	0·000,000,001
Cubic centimetre	=	0·000,001
Cubic decimetre	=	0·001
Cubic metre	=	1
Cubic decametre	=	1,000
Cubic hectometre	=	1,000,000
Cubic kilometre	=	1,000,000,000

Measures of Capacity.

Unit — 1 *litre* = *Decimetre cube.*

Millilitre	=	0·001 or $\frac{1}{1000}$th of a litre.
Centilitre	=	0·01 or $\frac{1}{100}$th „
Decilitre	=	0·1 or $\frac{1}{10}$th „
Litre	=	1
Decalitre	=	10
Hectolitre	=	100
Kilolitre	=	1,000

Measures of Weight.

Unit — 1 gramme = weight of 1 cub. centimetre of distilled water at 4°C. (weight of 1 litre of water = 1,000 grms.)

		Grms.
Milligramme	=	0·001 or $\frac{1}{1000}$th of a gramme.
Centigramme	=	0·01 or $\frac{1}{100}$th „
Decigramme	=	0·1 or $\frac{1}{10}$th „
Gramme	=	1
Decagramme	=	10
Hectogramme	=	100
Kilogramme	=	1,000

The measures of surface are devised on the same model, but are seldom employed in chemistry. They are, therefore, omitted here.

For the mutual conversion of weights and measures on this and on the old English systems, the following table will afford sufficient data :—

		Inches.	Feet.	Yards.
1 Metre	=	39·37079	3·280899	1·0936331
		Cub. inches.	Cub. feet.	Imp. gall.
1 Cubic metre, kilolitre, or stere	=	61027·05152	35·316581	220·0966767
			Imp. pint.	
1 Litre	=	61·02705	1·76077	0·2200967
		Grains.	Oz. Troy.	Lbs. Av.
1 Gramme	=	15·43235	0·032151	0·0022046

1 Inch = 2·539954 centim.
1 Cub. inch = 16·386176 cub. centim.
1 Gallon = 4·543458 litres.
1 Grain = 0·064799 grm.

The student should endeavour to remember that 1 metre =39·37 in., 1 litre = 61 cub. in., and 1 grm. = 15½ grs.,—as nearly as possible.

A myriometre, myriolitre, or myriogramme means 10 kilometres, kilolitres, or kilogrammes.

Specific Gravity.—That equal bulks of different forms of matter have different weights is a fact of every-day observation. A piece of iron, for instance, is very perceptibly heavier than the same bulk of wood; a cubic decimetre of platinum, the heaviest form of matter known, is 200,000 times as heavy as the same volume of hydrogen, the lightest substance yet discovered.

The specific gravity or density of a substance is the number which expresess the ratio of the weight of a given volume of this substance to that of an equal volume of some standard body.

Standards of Comparison. In England solids and liquids have hitherto usually been compared, as regards specific gravity, at the standard temperature of 15°·5 C. with distilled water at that temperature. In France the standard tempera-

ture is 0° C.—and the unit of density is pure water at 4° C. (its point of maximum density). The numbers obtained by these two methods of comparison differ only very slightly; but it is necessary to bear in mind that both methods are employed. The standard which we shall use in the case of gases and vapours is pure hydrogen. It was formerly usual to employ pure and dry atmospheric air. We shall sometimes have occasion to mention the numbers expressing specific gravities according to this old standard. These may, with the greatest facility, be converted into specific gravities on the hydrogen standard, if we remember that the specific gravity of atmospheric air is 14·45 when that of hydrogen is 1. The standard temperature employed for gases and vapours is either 15°·5 C. or 0° C. The latter is probably preferable. The standard of barometric pressure is 760 millimetres.*

DETERMINATION OF SPECIFIC GRAVITIES.—The slightest sketch of some of the methods by which specific gravities or densities are found must, for want of space, suffice.

Gases. A globe is weighed, after being exhausted of air by means of the air-pump; again when full of hydrogen at 0° C. and 760 mm. bar. pressure; and again when filled with the gas at the same temperature and pressure. The data for the following proportion are thus obtained:—

Weight of hydrogen : weight of gas :: 1 : sp. gr. of gas.

Liquids. A light bottle of known weight, accurately fitted with a stopper, is weighed when full of water at 4° C.; and again (after rinsing with the liquid) when filled with the liquid at 0° C. The weight of the bottle is deducted from both results; and then

Weight of water : weight of liquid :: 1 : sp. gr. of liquid.

Solids. The principle applied in the case of solids was discovered by Archimedes, and may be thus stated: *When a*

* Some account of the barometer will be found in chap. xii.

solid is immersed in a liquid and weighed, its weight is less than when weighed in air, and is less by exactly the weight of the liquid of which it has taken the place, in other words, *by the weight of its own bulk of that liquid.* To obtain the specific gravity—

(i.) *Of a solid body insoluble in water*—weigh in air, then suspend from the scale-pan of the balance by a horsehair, and weigh in water:

Loss of weight (or weight of equal bulk of water): weight in air :: 1 : sp. gr.

(ii.) *Of a solid body having a less sp. gr. than water.*—Weigh in air; attach to a substance the weight of which in water has been found, and which has sufficient weight to keep the light body under water; weigh in water; and deduct from the result of this weighing the ascertained weight of the heavy substance in water.

(iii.) *Of a powder* (*e.g.*, sand).—Take a bottle which contains when full a known weight of distilled water (say 100 grms.); put into it when empty a known weight (say 15 grms.) of the sand; fill up with water; weigh again; and suppose that the weight of water and sand in the bottle is found to be 109·6 grms.; of this 94·6 (109·6—15) grms. are due to water; 5·4 (or 100—94·6) grms. of water have therefore been displaced by the 15 grms. of sand:—

$$5{\cdot}4 : 15{\cdot}0 :: 1 : \text{sp. gr. of sand } (= 2{\cdot}77).$$

(iv.) *Of a solid body soluble in water.*—Substitute for water a liquid in which the substance is insoluble, and for 1 in the proportion the specific gravity of this liquid, adopting one or other of the above plans, according as the substance is heavier or lighter than the liquid, or is in a state of powder.

Precautions.—To obtain accurate results, the experimenter must observe many precautions, for which he is referred to works on physics, such as those of Dr. Miller and M. Ganot. Here it is only possible further to observe that a correction has often to be made for weighings taken in air, on account of

the application of the discovery of Archimedes just noticed to gases as well as to liquids; the weight of a body in air is less than its weight in the absence of air—*i.e.*, *in vacuo*,—by the weight of the air which it displaces, viz., of its own volume of air.

HEAT.—The rest of this chapter must be devoted to the subject of the force called heat, to the consideration of the nature, sources, &c., of which we now proceed.

*Nature of this Force. Heat is a form of motion of the ultimate particles of matter.** Many other forces also—and, perhaps, amongst these the chemical force to a certain extent —are other forms or modes of motion of the ultimate particles of matter.

The heat of a body is caused by an oscillatory motion of its material particles. Bodies are hottest when the vibrations of their particles have the greatest amplitude and the greatest velocity.

Relation between the Forces of Heat and Chemical Affinity. Heat is the most important of all agents in chemical change. Chemical combination is always attended with evolution of heat; though, if the liquefaction of a solid or of ice pent up in a solid accompany the action, the only apparent result may be the production of cold; as, for example, when warm sodic sulphate is mixed with warm hydrochloric acid, and intense cold is produced.

SOURCES OF HEAT.—The causes to which the manifestations of heat on the earth are due may, for our purposes, be enumerated under two heads: 1*st. Mechanical and Physical Sources*, such as friction, percussion, and pressure (all of which are forms of motion readily convertible into that motion which we call heat), radiation from the sun (the cause of whose heat is unknown), terrestrial heat (probably due to the molten condition of the earth's interior), changes from the gaseous to the liquid, and from the liquid to the solid state, electricity, &c.

* Heat as a mode of motion, § 20.

2nd. Chemical Sources, viz., all forms of combination, and notably those forms to which we apply the term "combustion" (v. chap. xii).

EFFECTS OF HEAT.—The weight of bodies is not affected by heat any more than by either cohesion or chemical affinity. But many physical properties of matter—such as bulk, hardness, elasticity, luminosity, &c.—are altered by heat.

Expansion. As a rule, all bodies expand—or increase in bulk—under the action of heat. But there are a few exceptional cases in which, between certain temperatures, some substances contract when heated; *e.g.*, water from 0° C. to 4° C.

Expansion of Gases. Gases expand more than liquids or solids. For every degree on the centigrade thermometer they expand about ·3665 per cent.; so that 100 volumes of atmospheric air, for example, measured off at 0° C., become 100·3665 volumes at 1° C., 100·733 volumes at 2° C., and so on;—or air which occupies one volume at 0° C. occupies 1·003665 vol. at 1° C., 1·00733 vol. at 2° C., &c.

The following laws are approximately—but not rigorously true:—

i. *The coefficient of expansion of air is* ·003665.

ii. *All gases have almost precisely the same coefficient of expansion as air.*

iii. *This coefficient is the same whatever be the pressure supported by the gas.**

Expansion of Liquids. Liquids, as a rule, expand much less than gases, and not nearly so regularly. But some condensed or liquefied gases expand even more rapidly than air. The *apparent expansion* of a liquid is the visible expansion observed when the vessel in which it is contained also expands, as in the case of the bulb and tube of a thermometer. The *absolute expansion* is the real increase of volume the liquid undergoes. The following table affords a few examples of the

* Ganot's Physics, p. 217.

APPARENT EXPANSION OF LIQUIDS BETWEEN 0° C. AND 100° C.

Mercury	0·01453	Ether	0·07
Distilled water	0·05	Fixed oils	0·08
Sulphuric acid	0·06	Nitric acid	0·11
Hydrochloric acid	0·06	Alcohol	0·116

Owing to the irregularity of the expansion, the coefficient of expansion obtained by dividing these numbers by 100 does not express the amount of expansion between every pair of degrees on the scale. The rate of expansion usually increases gradually, from zero upwards.*

Expansion of Solids. Solids are still less expansible, and still more irregular in their expansion. In them the *linear dilatation*, or expansion in one direction, must be distinguished from the *cubical dilatation*, or expansion in volume. The *coefficient of linear dilatation* is the elongation of the unit of length of a body when its temperature rises from 0° to 1°; and the *coefficient of cubical dilatation* is the increase of the unit of volume under the same circumstances.† The total expansion, linear and cubical, which various solids undergo between 0° and 100°, is shown in the following table:—

EXPANSION OF SOLIDS FROM 0° TO 100° C.

	In length.	In bulk.
Flint glass	1 in 1248	1 in 416
Platinum	1 „ 1131	1 „ 377
Steel	1 „ 926	1 „ 309
Iron	1 „ 846	1 „ 282
Gold	1 „ 682	1 „ 227
Copper	1 „ 582	1 „ 194
Brass	1 „ 536	1 „ 179
Silver	1 „ 524	1 „ 175
Tin	1 „ 516	1 „ 172
Lead	1 „ 351	1 „ 117
Zinc	1 „ 340	1 „ 113

* Ganot's Physics, p. 213.

† Ib., p. 202.

TEMPERATURE.—The terms *heat* and *temperature*, when accurately employed, should convey very different ideas.

The *heat* of a body, or the *quantity of heat* which it is said to contain, is the actual quantity of this force which it can give up to other bodies.

The *temperature* of a body, on the other hand, is that perceptible heating effect which this body exerts, by the motion of its own particles, on surrounding objects—on men's organs of sense, for example; and temperature is measured by these effects either on the sense of touch, or on delicate instruments, called *thermometers*.

In illustration of one distinction between the words *heat* and *temperature*, we may cite this example:—If a litre of water has the same temperature as a kilolitre, the quantity of heat, or the amount of force stored up in the kilolitre, is evidently not the same, but a thousand times greater.

Thermometers are, as we have stated, instruments for measuring temperature; the principle on which they effect their object is the expansion of solids, of liquids, or of gases, under the influence of heat, and their contraction on the reduction of their temperature. We shall not here find it necessary to notice any thermometers but such as depend on the expansion and contraction of liquids. The liquids commonly employed in thermometers are mercury and alcohol.

The Mercurial Thermometer is the more useful, both because the expansion of mercury is very regular, and proportional to the rise in temperature, for every degree between − 36° C. and 100°,—and because the "specific heat" (v. pp. 26, 31) of mercury is very low. This thermometer cannot be used for temperatures above 350°, as this is the boiling point of mercury.

The Alcohol Thermometer is filled with coloured alcohol and has these advantages: that alcohol does not solidify at the greatest known cold, and that for each degree the expansion of alcohol is nearly nine times as great as that of mercury. But at all temperatures, especially those above the normal

temperature of the atmosphere, its expansion is very irregular, and at 78° C. it boils.

Construction of a Thermometer. To make a mercurial thermometer, take some capillary glass tubes, and, in order to select one which is of the same diameter and quite cylindrical throughout, or equal parts of which are of equal capacity, introduce a thread of mercury about an inch long, and move it about in the tube, taking care not to alter its temperature. If the thread is not of the same length in every part of the tube, the capacity cannot be everywhere the same, and the tube must be rejected. This is called the "calibration" of the tube. Otherwise, at one end of the tube selected a bulb must next be blown, and at the other an enlargement or small funnel is made. When the bulb has been gently heated, so as to expand and partly expel the air in the bulb and tube, the other end of the tube is immersed in mercury, which rises into the cooled tube and bulb, to take the place of the expelled air; another warming of the bulb drives out more air, which is replaced by mercury, as before; then the mercury—which by this time fills the bulb and nearly the whole tube—is heated till the upper part of the tube is full of mercurial vapour; a final immersion of the open end in mercury causes the condensation of this vapour and its complete replacement by mercury; the mercury is now very carefully heated till it reaches its boiling point, when the tube is closed by drawing off the stem, at the upper enlargement or funnel, in the blowpipe flame. When the thermometer becomes cold, the mercury will have contracted, and will fill the bulb and a portion only of the stem. The remainder of the stem ought to enclose a tolerably perfect vacuum containing a little vapour of mercury and no air.

Graduation of a Thermometer. It is well to keep the thermometer for six months or a year before proceeding to graduate it; for it has been found that, owing probably to the pressure of the atmosphere, the bulb gradually contracts for some time after the stem has been closed. The bulb, with part of the stem of the thermometer, is then immersed in

melting pounded ice or snow; and at the level of the mercury a mark is made which is the zero of the scale—(0°)—and represents the freezing point of water, or the melting point of ice, a point which is constant at all atmospheric pressures. The next point to determine—(100°C.)—is the boiling point of water at the ordinary atmospheric pressure. This is found by placing the thermometer in an apparatus in which the bulb and part of the stem are suspended just above the surface of boiling water in its vapour. The bulb should not be immersed in the water, as impurities in solution, the material of the vessel, &c., affect the boiling point of water, though they have no influence on the temperature of the vapour formed. When the mercury has ceased to expand, the point at which it remains stationary is marked. But the height of the barometer at the time must also be observed, and, if it is either greater or less than 760 mm., a correction must be made; for at high atmospheric pressure the boiling point of water is above 100°C.; at low pressure it is below this point. For every 27 mm. difference in the barometric height, there is in the boiling point a difference of 1° C. The interval between the two points thus determined is now divided into a hundred degrees, and degrees of equal length are marked off on the remainder of the stem and numbered.

Thermometric Scales. In this way a thermometer is made according to the *centigrade* scale invented by Celsius, and now almost exclusively adopted for scientific purposes.—Two other scales are, however, frequently used: Fahrenheit's, in which the temperature at which water boils is called 212°, whilst the freezing point is 32°; and Réaumur's, in which the zero corresponds to the centigrade zero, but the interval between this point and the boiling point of water is divided into *eighty* degrees.

Fahrenheit fixed his zero, which is 32° F. below the freezing point of water, at the lowest point to which he succeeded in bringing the mercury by means of a mixture of snow and sal-ammoniac. When he had produced this low

temperature he is said to have thought that no heat was left; and he called the point zero. This zero happened also to indicate the most intense cold which had been observed in Iceland. It need hardly be said that much lower temperatures, natural and artificial, have since been observed. Unfortunately, this scale is still much used in England, Holland, and North America. Réaumur's scale continues in use in Germany and Russia.

As the fixed points taken in all these divisions are the same, and as 100° on the centigrade scale are equivalent to 180° on Fahrenheit's and 80° on Réaumur's scale, it is easy to reduce degrees on one system to degrees on either of the others by means of a simple calculation represented by the following equations:—

$$C = \frac{5(F - 32)}{9}; \qquad F = \frac{9C}{5} + 32;$$

$$C = \frac{5}{4}R; \qquad R = \frac{4}{5}C.$$

In performing this operation the student must not neglect to take the *minus* sign into account. For instance, to convert 5° F. into centigrade degrees, we say—

$$C = \frac{5(5 - 32)}{9} = -15°.$$

Chapter III.

SPECIFIC, LATENT, AND RADIANT HEAT, &c.

Specific Heat.—In agreeing upon a definition of *heat* we have had occasion to observe that this and many other forces are forms of motion. Now, it is a fact which scientific investigation has placed beyond all doubt that all force is indestructible, and that all motion is perpetual;* but just as the motion imparted to a rifle-ball by the explosion of a charge of gunpowder seems to be at an end as soon as it is arrested by the target and to be anything but perpetual, so the mode of motion called heat appears to be easily arrested and destroyed. But if we examine these phenomena a little more closely, we shall observe that the air through which the bullet passed is set in motion, and also to some extent (however slightly) heated, that the bullet itself has been heated, that the target has been heated, and that when the bullet struck the target, a sound (another form of motion) was produced; and all these several modes of motion will, when examined and added together, be found exactly to amount to the original motion of the bullet; so that this original motion resolved itself into the several kinds of force or motion enumerated. And so it is in the case of any other form of motion such as heat. If heat apparently disappears, the motion only takes some other form, such as electricity or sound, for example. Thus that portion of the *quantity of heat* in a body which is not evident to our senses, but which, owing to the *indestructibility and conservation of force*, must still be doing mechanical work within it, is employed in overcoming the force of co-

* Miller's Chemistry, vol. i, p. 569. Heat as a mode of motion, § 155.

hesion—in compelling the atoms of the body to take up new positions—in expanding, in liquefying, or in vaporising the body.

To quote Professor Tyndall's words: The heat imparted to a body (a piece of lead, for example) "is applied to two distinct purposes—it performs two different kinds of work. One portion of it excites that species of motion which augments the temperature of the lead, and which is sensible to the thermometer; but another portion of it goes to force the atoms of lead into new positions, and this portion is *lost as heat.*"*

In this case, then, of the piece of lead, continues Professor Tyndall, "the heat not only imparts actual energy to the vibrating atoms, but also accomplishes what we may call *interior work;* it performs work within the body heated by forcing its particles to take up new positions. When the body cools, the forces which were overcome in the process of heating come into play, and the heat which was consumed by the forcing asunder of the atoms is now yielded up by their falling together."†

Chemistry teaches us that the atoms of different bodies have different weights, the relations between which have been determined. Thus an atom of oxygen weighs as much as 16 atoms of hydrogen; but, on the other hand, it seems extremely probable that the possession of exactly the same amount of heat at the same temperature is characteristic of every elementary atom, whatever may be its weight. Hence at 0°, at 15°, at 30°, and at all temperatures, an atom of hydrogen possesses the same quantity of heat as an atom of oxygen, and one gramme of hydrogen the same quantity as 16 grammes of oxygen, or 16 times as much as one gramme of oxygen.‡ This law is subject to the following important limitations: the amount of heat possessed at the normal tem-

* Heat as a mode of motion, § 159.

† Ib., § 160.

‡ Ib., § 161.

perature by the atoms of elementary permanent gases is uniformly less than that of solid atoms, since no sensible interior work has to be performed in gases; again, liquefiable elementary gases and vapours possess abnormal amounts of heat near their points of liquefaction.

To raise one gramme of hydrogen a certain number of degrees in temperature—say from 10° to 15°—would require sixteen times the amount of heat needed by a gramme of oxygen under the same circumstances. Conversely, a gramme of hydrogen, in falling through 5°, would yield sixteen times the amount of heat yielded by a gramme of oxygen in falling through the same number of degrees.*

In solid and liquid bodies, besides these differences due to the number of atoms present in the unit of weight, there are also differences due to the consumption of heat in interior work. Hence it is clear that the absolute amount of heat possessed by a body is not at all declared by its temperature. To raise a kilogramme of water one degree requires about thirty-two times the amount of heat necessary to raise a kilogramme of mercury one degree. Conversely, the kilo. of water, in falling through one degree, yields thirty-two times the amount of heat yielded by the kilo. of mercury.† We therefore say that the capacity for heat, or the specific heat, of water is 32 times as great as that of mercury.

Hence the "*specific heats*" or "*capacities for heat*" of different substances are those numbers which express the relative amounts of heat given out by a unit of weight of each solid, liquid, or gas in cooling from some given temperature to another given point—(say from 100° to 0°)—the specific heat of water, the standard of comparison, being taken as unity.‡ Three methods are employed for determining these numbers; it will be convenient to postpone the description of these methods till we have considered the subject of so-called

* Heat as a mode of motion, § 162.
† Ib., § 163.
‡ Ib., § 165.

LATENT HEAT.—Under the head of specific heat it has been our province to speak only of the consumption or evolution of heat observed in the molecular changes of solid, liquid, or gaseous bodies, *whilst these bodies continue solid, liquid, and gaseous respectively.* The phenomena which accompany *changes of the state of aggregation* must now in turn engage our attention.*

When heat is communicated to a substance, and, instead of increasing the temperature of that substance, disappears, ceasing for the time to affect the thermometer, it is said to become *latent.* This takes place whenever matter passes from the solid to the liquid, or from the liquid to the gaseous state; for example:—If you fix a thermometer in a block of ice having a temperature of — 5°, and warm the ice in a clean open vessel, the thermometer rises to zero, and at this point the ice begins to melt; but the thermometer remains stationary, and, though you continue to apply warmth, the temperature does not augment; at length the last particle of ice melts, and then the column of mercury resumes its rise, reaching successively 20°, 40°, and 60°, and so on up to 100°, when the water begins to boil; you continue to apply heat, but again the thermometer refuses to rise, and, till the whole contents of the vessel have been converted into steam, remains fixed at 100°.

Again, when one kilo. of water at 80° is added to another kilo. of water at 0°, a mixture having a temperature of 40° is produced:—but one kilo. of ice at 0° mixed with one kilo. of water at 80° gives two kilos. of water at 0°. Hence the mere conversion of a kilo. of ice into a kilo. of water at the same temperature requires an amount of heat sufficient to raise a kilo. of water through 80°. This quantity of heat is called the *latent heat of fusion* of ice, or the latent heat of water.

When water at 15° is exposed to an intense cold, say — 40°, it cools down to 0°, begins to freeze, and remains at that temperature till it is completely solid, when the temperature

* Heat as a mode of motion, § 176.

of the ice again proceeds to sink to — 40°. Whilst solidification was progressing, latent heat of water, or the latent heat of fusion of ice, was extricated; and consequently the temperature did not fall till the source of this heat had been exhausted by the congelation of the last drop of water.

We have seen that when water is heated in an open vessel its temperature rises to 100°, when it begins to be converted into steam; and that its temperature, heat the water as you will, will not rise above 100°; in this case the heat said to be rendered latent is called the *latent heat of evaporation* of water, or the latent heat of steam.

The heat expended in melting ice or vaporising water is really consumed in moving—in conferring energy upon—the atoms. The act of fusion or liquefaction consists of interior work. That of vaporisation is also partly interior work, and partly the work of forcing back the atmosphere with a power greater than the atmospheric pressure, a species of exterior work which the vapour into which the heat resolves the liquid has to accomplish.*

The following are further examples of the apparent disappearance of heat when changes of the state of aggregation from the solid to the liquid, or from the liquid to the vaporous state take place:—When solids, such as sugar, salt, or—better—saltpetre, are made to dissolve in water, a fall of temperature may be detected. Warm sodic sulphate and warm hydrochloric acid form a powerful freezing mixture. The evaporation of ether, even when previously warmed, produces a marked fall of temperature, and sometimes a cold so intense as to be applicable in surgery to the numbing of a part on which an operation is to be performed. Porous earthenware bottles, admitting of constant evaporation of their contents at every point of their surface, are used to cool drinking-water. Liquid carbonic anhydride can only be preserved under great pressure; when released from confinement it boils with great

* Heat as a mode of motion, §§ 177, 178.

violence, and becomes partly converted into gas; but the cold produced in this transition is so severe that the other portion solidifies. Even water can be frozen in this way by means of its own evaporation; this may readily be effected in the *cryophorus* (κρυός, frost, φορός, bearing), an instrument invented by Dr. Wollaston, and constructed as follows:—A bulb is blown at one extremity, and a second close to the other end of a glass tube a few inches long; a small tube terminating in a minute orifice is drawn out from the latter bulb; at two points, near the bulbs, the tube joining them is bent at right angles; into the terminal bulb a little water is introduced; and this is boiled till the air in the instrument has been completely expelled by steam, when the orifice must be sealed in the blow-pipe flame; one of the bulbs is now about half full of water, the vapour of which fills the connecting tube and the other bulb; the latter must now be immersed in a freezing-mixture so as to condense the vapour it contains. The pressure is thus reduced; the water in the further bulb (which should be protected from currents of air) yields fresh vapour and parts with more and more of its heat, till its temperature reaches zero, and it is converted into ice.

Again, in changes from the liquid to the solid state, such as crystallisation, and in all experiments in which a gas or vapour is converted into a liquid or a solid, a rise of temperature, due to the evolution of heat which has been performing interior work, may be observed. Water may be cooled to a temperature considerably below zero, without freezing, if preserved with care from agitation; but the slightest disturbance enables the solidification to commence, and this is always accompanied by the rise of the temperature to 0°.

Calorimetry has for its object to measure the *quantity of heat* which a body gives out when its temperature falls, or absorbs when its temperature rises, through a certain number of degrees, or when it changes its physical condition.* It

* Ganot's Physics, p. 279.

has, therefore, two departments, the measuring of specific and the measuring of latent heat.

Modes of Measuring Specific Heat. i. Mixtures. When two equal volumes, at different temperatures, of the same liquid are mixed together with care, the temperature of the whole is always exactly the mean of the two; *e.g.*, mix a litre of water at 15° with a litre at 45°, and the resulting temperature is 30°. But, if different liquids are used, the temperature obtained is not the mean; and, if equal weights instead of equal volumes of the different bodies be mixed, the result is still further removed from that which equal volumes of the same liquid produce; *e.g.*, if a kilogramme of mercury at 100° be mixed with the same weight of water at zero, the temperature of the mixture will be scarcely more than 3°; so that to raise the water only about 3°, the mercury has been cooled through about 97°, or about 32 times the number of degrees. Hence to produce the same rise of temperature, water evidently requires about 32 times as much heat as an equal weight of mercury. Thus, the fact stated above that the specific heat of water is approximately 32 times as great as that of mercury is proved; and, if the specific heat of water is 1, that of mercury is 0·033.—This method of mixtures is the best mode of determining specific heats.

ii. By ascertaining the *rate of cooling* of equal weights of different bodies, their specific heats may be found; but the difficulties in the way of accurate results have been a serious objection to the employment of this method.

iii. Another method consists in discovering what weights of ice given weights of various substances will melt, when cooled from one fixed temperature to another, say from 100° or 80° to zero or 15°. Lavoisier and Laplace's *calorimeter* is used in experiments of this nature; it consists of three concentric tin vessels, two of which are filled with pounded ice, whilst in the central one the body whose specific heat is to be found, heated to the required temperature in an oil- or water-bath, is placed. The outer vessel is intended for the protec-

tion of the essential part of the apparatus from the warmth of the atmosphere. The water due to the melting of the ice in the second vessel by the heated body is run off through a stopcock and weighed. A kilogramme of water in cooling from 80° (more accurately according to M. Person 79°·25) to 0° gives off enough heat to melt one kilo. of ice; or one kilo. of ice, in melting, absorbs 80 times the quantity of heat necessary to raise the temperature of one kilo. of water 1° (or, as it is expressed, a kilo. of ice, in melting, absorbs 80 *thermal units*). Hence—since the specific heat of water is taken as unity—if the amount of ice melted by a kilo. of any other body, in cooling from 80° to zero, be determined to be Q kilos., the specific heat of the body is Q.

Mean specific heats of solids and liquids between 0° *and* 100°. By means of the first and third methods, M. Regnault has determined the specific heats of a number of bodies; the following are examples:*—

Substances.	Spec. Heats.	Substances.	Spec. Heats.
Water	1·00000	Nickel	0·10863
Turpentine	0·42590	Cobalt	0·10696
Calcined animal charcoal	0·26085	Zinc	0·09555
Wood charcoal	0·24111	Copper	0·09515
Sulphur	0·20259	Brass	0·09391
Graphite	0·20187	Silver	0·05701
Thermometer glass	0·19768	Tin	0·05623
Phosphorus	0·18949	Antimony	0·05077
Diamond	0·14687	Mercury	0·03332
Grey iron	0·12983	Gold	0·03244
Steel	0·11750	Platinum	0·03243
Iron	0·11379	Bismuth	0·03084

Specific Heats of Gases and Vapours. These are found by causing a measured volume of each gas under constant pressure and at a given temperature to pass through a spiral glass

* Ganot's Physics, p. 341.

has, therefore, two departments, the m
and the measuring of latent heat.

Modes of Measuring Specific Heat. ' two equal volumes, at different temperat liquid are mixed together with care, the whole is always exactly the mean of the tv of water at 15° with a litre at 45°, and the ture is 30°. But, if different liquids are use obtained is not the mean; and, if equal w equal volumes of the different bodies be mix still further removed from that which equa same liquid produce; *e.g.*, if a kilogramme o be mixed with the same weight of water at z ture of the mixture will be scarcely more tha raise the water only about 3°, the mercury through about 97°, or about 32 times the num Hence to produce the same rise of temperat dently requires about 32 times as much hea weight of mercury. Thus, the fact stated a specific heat of water is approximately 32 time that of mercury is proved; and, if the specific is 1, that of mercury is 0·033.—This method of m best mode of determining specific heats.

ii. By ascertaining the *rate of cooling* of equa different bodies, their specific heats may be foun difficulties in the way of accurate results have bee objection to the employment of this method.

iii. Another method consists in discovering wh of ice given weights of various substances will m cooled from one fixed temperature to another, say or 80° to zero or 15°. Lavoisier and Laplace's *cal* used in experiments of this nature; it consists of t centric tin vessels, two of which are filled with pour whilst in the central one the body whose specific heat found, heated to the required temperature in an oil- or bath, is placed. The outer vessel is intended for the

Besides barometric pressure, other circumstances, such as the presence of substances dissolved, and the nature of the vessel, influence the boiling-point of a liquid. This may be illustrated by the effects of these causes upon distilled water, the boiling-point of which at 760 mm. pressure is, as we have seen, 100°.

When saturated with various salts, water boils at the following temperatures:*—

Sodic carbonate	104°	Sodic nitrate	121°
Potassic chlorate	104°	Potassic carbonate.....	135°
Sodic, or potassic chloride..	108°	Calcic nitrate.....	151°
Sal-ammoniac	114°	Potassic acetate.....	169°
Potassic nitrate.....	116°	Calcic chloride	179°

Water carefully freed from dissolved air may be raised to a high temperature without boiling, till finally it bursts into vapour with explosive force.

If the surface of the vessel in which the water is boiled be such that the water has a tendency to adhere to it, this water may be raised to a temperature higher than 100° without boiling. Water boils in a copper vessel at 100°, in a glass vessel at 101°; and, if the glass vessel has been cleaned with strong sulphuric acid and potash, or varnished with shellac, water refuses to boil in it till a temperature of 105° is attained. In these cases a little bit of metal dropped into the water will always reduce the temperature to 100°, and at this point ebullition will continue. A piece of metal is frequently employed with this object, and with a view to the prevention of the violent and dangerous succussions which accompany the ebullition of liquids in glass vessels.

But the temperature of the aqueous vapour or steam disengaged, so long as the barometric pressure is 760 mm., is always 100°, however the point at which ebullition commences may be affected either by the nature of the vessel or by the substances dissolved. Hence, if the rule of immersing the

* Miller's Chemistry, vol. i, p. 293.

thermometer in the vapour, and not in the boiling liquid, be observed, boiling-points may be determined in vessels of glass or any other material.

EVAPORATION.—The passage of a liquid into the vaporous or gaseous condition—its *vaporisation*—takes place, not only in the rapid manner just described, but also slowly at the surface of liquids. The latter kind of vaporisation receives the name of *evaporation*. It does not, like ebullition, proceed only at some fixed definite temperature; a liquid will evaporate below its boiling-point at all temperatures, down to a certain point where the formation of vapour seems to cease; for mercury this point is — 10°, and for sulphuric acid 30°. The rapidity of evaporation of a liquid is affected by four circumstances:—1. The temperature, the increase of which accelerates evaporation, by increasing the elastic force of the vapours. 2. The quantity of the same vapour in the surrounding atmosphere, the saturation of which with this vapour would stop evaporation. 3. The renewal of the atmosphere, so as to prevent its saturation. 4. The extent of the surface of evaporation.* In different liquids the amounts of vapour given off at a constant temperature are very different, and depend on their boiling-points, which, as we have observed, are the points at which their vapours severally possess an elasticity or tension equal to that of the atmosphere. Hence the volatility of a liquid is dependent on the tension or elasticity of its vapour; and this is measured by the height of the barometric column of mercury (v. inf. p. 114), which the pressure of the vapour will support. At the boiling-point of a liquid, therefore, the tension of its vapour is 760 mm.

CONVECTION.—When gases and liquids—the forms of matter in which the particles are freely mobile—are heated, the heated particles rise, and their places are taken by cooler particles, which in turn rise, and are similarly replaced. This process of transferring heat from place to place by particles

* Ganot's Physics, pp. 230, 240.

or sensible masses of matter is called "*convection.*" The motion which we call wind in due to convection (v. p. 117). In order to heat liquids we always make use of convection. If heat be applied at the bottom of a flask or beaker containing water, the heated particles ascend in a central column, while cold particles supply their places from the sides. If some fragments of bran, or of cochineal, are thrown into the water, they will be seen to follow the currents of convection, rising through the middle of the flask, and again descending by the sides.

CONDUCTION.—We should now be able to distinguish between the sensible motions produced by heat—the *mechanical* motions into which heat may be converted—and heat itself, a form of *molecular* motion. This molecular motion must, when the particles of a body are closely grouped, be communicated from one to the other.*

A steel poker, the end of which has been allowed to remain for a time at a red heat in a fire, burns the hand of any one who ventures to touch its handle. This is due to the propagation of the molecular motion in the manner just explained, till the heat of the red-hot end of the poker has been transmitted through its whole length to the handle. This kind of transmission of heat is called *conduction.* Different substances conduct heat with very different degrees of rapidity. A steel poker may be handled with impunity after its extremity has remained in a hot coal fire for ten minutes; but a poker made of silver would be so hot at the end of half that time that it would not be easy to remove it. Silver is a very *good conductor* of heat. Bars of glass, wood, and many other substances conduct heat far more slowly than iron or steel bars. The molecules of glass, wood, stone, fire-clay, and other *bad conductors* are incompetent to pass the molecular motion freely from one to another.† The relative powers possessed by different substances, as compared with silver,

* Heat as a mode of motion, § 242.

† Ib., § 244.

for the conduction of heat are called their conductivities. These have been investigated by Wiedemann and Franz. The following are examples of their results:*—

Silver	100	Iron	12
Copper	74	Lead	9
Gold	53	Platinum	8
Brass	24	German silver	6
Tin	15	Bismuth	2

Liquids and gases are, as we have observed, usually heated by convection. When any precaution to prevent this transport of heat by their mobile particles is adopted, it is found that liquids cannot readily be heated by conduction. In fact, the conductivity of liquids is excessively feeble, whilst it is doubted whether gases possess this conducting power in any degree.

RADIATION.—The vibrations or oscillations of heat are also transmitted from place to place in another and totally different manner, analogous to that in which those other forms of motion, light and sound are conveyed. In the same manner that rays of light reach us from the sun, or from any other source of heat, such as an open fire, rays of heat bring to us the heat emitted from the sun, or from the burning coals. We can here notice but briefly the fact that heat also exists in this condition, propagated with the velocity of light (according to Le Verrier, 183,470 miles in a second), and capable of passing through interstellar space as well as through vacua artificially produced. Heat in this condition is distinguished as heat in the *radiant* state, *radiant heat.* For the study of radiant heat and of the laws which it obeys, the reader is referred to the last six chapters of Professor Tyndall's "Heat considered as a Mode of Motion."

* Heat as a mode of motion, § 247.

Chapter IV.

HYDROGEN, H_2.

Atomic Weight and Sp. Gr. = 1. *Molecular Weight* = 2. *Molecular Volume* $\square$. 1 *litre weighs* 1 *crith*. *Equivalence* 1.*

Occurrence. This element (ὕδωρ, water; γεννάω, I produce) was discovered by Cavendish in 1766, and called by him "inflammable air." As it is one of the two constituents of water, and is necessarily present in large proportion in all animals and plants, it is a very important element. Free hydrogen has been proved to exist in many of the heavenly bodies, and Mr. Graham recently made the remarkable discovery that it is frequently present in meteorites, absorbed in the pores of the metals of which they are composed.

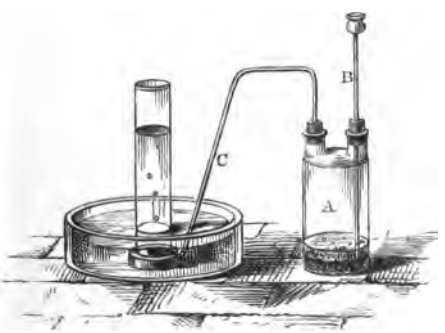
Preparation. 1. *Best Method:* The action of metallic zinc on diluted sulphuric acid. Place some pieces of zinc either in a bottle (fig. 1,—A), with two necks—or in a small flask of thin glass, provided with a tight-fitting cork, with two perforations—for a funnel, B, which reaches nearly to the bottom of the flask, and for a delivery tube, C. Through the funnel introduce some dilute sulphuric acid; a brisk action is at once set up; the hydrogen of the acid is replaced by zinc, and zincic sulphate (or sulphate of zinc) is formed, whilst the hydrogen set free escapes. This is represented in symbols by the following formula:—

* The meanings of these terms and figures will be explained in Chapters V and VI.

$$\underset{\text{Sulphuric acid.}}{SO_4H_2} + Zn = \underset{\text{Zincic sulphate.}}{SO_4Zn} + H_2.$$

Iron may be used instead of zinc, but the gas produced is not so pure. When the gas has been coming off for such a length of time that you are quite sure that every trace of atmospheric air has been swept out of the flask and delivery tube, collect the gas over water, by immersing the delivery tube under water and placing over it an inverted jar or bottle quite full of water. The gas bubbles up into the vessel and displaces the water which it contains. Pneumatic troughs are convenient when many jars are to be filled with gas. Sometimes the gas is conducted into a gas-holder, such as that represented in fig. 2, where it may be kept stored up for use. For ordinary purposes a shallow tub of water or a basin answers quite well.

FIG. 1.

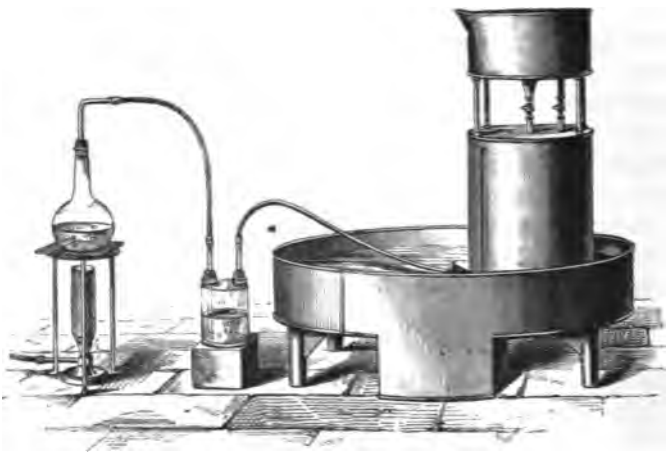


When a jar has been filled with gas it may be removed, a plate of ground glass, greased so as to prevent any escape, having first been placed over its mouth.

If absolutely pure hydrogen be required, use the purest zinc and acid that can be obtained, and pass the gas through a solution of potash, to absorb acid, through a solution of argentic nitrate (or nitrate of silver), to arrest arsenic, and,

lastly, through strong sulphuric acid, which abstracts moisture.

FIG. 2.



2. To obtain hydrogen cheaply, in large quantities, pass steam through a piece of iron piping containing iron nails or turnings, placed in a furnace and maintained at a red-heat. The gas so prepared contains much steam, part of which may be removed by passing the gas through tubes containing pieces of calcic chloride (chloride of calcium), a substance which attracts moisture powerfully. On a small scale hydrogen may be completely freed from moisture by passage through tubes containing phosphoric anhydride. The following equation represents the action of the iron on the steam :—

$$\underset{\text{Steam.}}{4OH_2} + Fe_3 = \underset{\text{Triferric tetroxide.}}{Fe_3O_4} + 4H_2.$$

One litre of water converted into steam will yield about 1240 litres, or 1·24 cub. metre of hydrogen.

3. Zinc or iron when heated with a strong solution of potassic or sodic hydrate, displaces hydrogen thus:—

$$\underset{\text{Potash.}}{2OKH} + Zn = \underset{\text{Zincic oxide.}}{ZnO} + \underset{\text{Potassic oxide.}}{OK_2} + H_2.$$

4. Deville and Debray prepare hydrogen on a large scale, by transmitting steam over charcoal or coke, heated to dull redness. When the temperature is kept sufficiently low, hydrogen and another gas, carbonic anhydride, are the only products:

$$\underset{\text{Water.}}{2OH_2} + C = 2H_2 + \underset{\text{Carbonic anhydride.}}{CO_2}$$

On passing these gases through an apparatus filled with slaked lime, the carbonic anhydride is readily absorbed, and pure hydrogen passes on. If the temperature of the charcoal be allowed to rise too high, carbonic oxide also is formed, and this gas cannot, practically, be removed.

The second and fourth processes depended on the decomposition or analysis of water in the state of vapour,—those which follow depend on its decomposition in the ordinary liquid condition; these are not practically important, but possess great theoretical interest.

5. The *electrolysis* of water. If a voltaic current be passed through water its constituent elements are liberated with effervescence,—hydrogen at the negative, oxygen at the positive pole.

$$2OH_2 = 2H_2 + O_2.$$

The decomposition is assisted by the addition of a few drops of acid to the water.

6. Owing to their great affinity for oxygen, the metals sodium and potassium have the power of decomposing water. They liberate part of the hydrogen and take its place:

$$Na_2 \text{ (or } K_2) + \underset{\text{Water.}}{2OH_2} = \underset{\text{Soda.}}{2OHNa} \text{ (or } \underset{\text{Potash.}}{2OHK}) + H_2.$$

A piece of potassium thrown on water ignites, glides about with a hissing noise, and causes the hydrogen evolved to burn with a violet flame. Sodium acts similarly, but not so violently, and, unless its motion be arrested (by a floating piece of blotting-paper, for instance, when it produces a flame of bright yellow colour), does not ignite the hydrogen given off; it is more easily manipulated than potassium, and a piece of sodium held under water, beneath the mouth of an inverted jar, by means of a spoon of wire-gauze, may be used for collecting a small quantity of hydrogen. Or a piece of the metal is pressed into a glass tube closed at one end, and is allowed to sink to the bottom of the pneumatic trough, so that the bubbles of hydrogen rise into a jar at the surface.

Properties. Hydrogen, when pure, is a transparent, colourless, tasteless, and inodorous gas. It is the lightest form of matter known. Atmospheric air is nearly 15 times as heavy as hydrogen, its specific gravity on the hydrogen scale being 14·45, whilst that of oxygen is 16. At 0° C. and 760 mm. bar. pressure 1 litre of hydrogen weighs 0·08961 grm. (or 1 *crith*). In other words, 11·15947 litres weigh one gramme. If the specific heat of water be taken as unity, that of hydrogen is 3·409. Hydrogen is a bad conductor of sound; a bell rung in an atmosphere of hydrogen is but faintly audible. Owing to its excessive lightness and the great mobility of its particles, hydrogen has a *diffusive power* higher than that of any other known substance. To make this statement intelligible, an explanation of the term *diffusion* is necessary. *Diffusion*—or the intermixture of one gas with another—sets in whenever two gases, even of different specific gravity, and although so arranged that the heavier gas is in the lower position, are brought in contact; and the gases continue to diffuse till the mixture is perfectly uniform throughout. Many liquids of different densities—such, for instance, as water and oil or

mercury—will not mingle naturally in this manner, and, even when artificially mixed by agitation, separate as soon as the agitation ceases. Gaseous diffusion takes place also if the gases are separated from each other by means of any dry porous substance, such as plaster of Paris, stucco, or thin plates of compressed graphite. Different gases have different rates of diffusion, and Mr. Graham has proved the following to be the *law of diffusion*:—The velocity of diffusion of a gas (or its *diffusion volume*) is inversely proportional to the square root of its density; so that, the density of hydrogen being 1 (the square root of which is 1) and that of air 14·45 (the square root of which is about 3·8), the diffusion volume of hydrogen is to that of air as 3·8 to 1; or whilst 3·8 measures of hydrogen mix with air, only 1 measure of air will, under the same circumstances, diffuse into hydrogen. This may be illustrated by leaving hydrogen in a cracked bottle, or in a tube one end of which is closed by plaster of Paris or some other porous substance, over water. The hydrogen will pass out so much more rapidly than the air passes in, that the water will rise within the vessel. Hydrogen refracts light more powerfully than any other gas; even when compressed till it has the same specific gravity as atmospheric air, it has a refractive power upon light more than six times greater than that possessed by atmospheric air. It has never been liquefied. Between 0° and 20° C., at the normal barometric pressure, 100 volumes of water are said by Bunsen to absorb 1·93 volumes of hydrogen.

Pure hydrogen is a non-supporter of life or combustion, but burns on ignition in air with a pale yellowish flame, which emits very little light, though great heat; the only product of the combustion is water : $2H_2 + O_2 = 2OH_2$.

A mixture of two volumes of hydrogen with five volumes of atmospheric air, explodes violently on ignition by means of heat or the electric spark, and nitrogen remains. Two volumes of hydrogen mixed with one volume of oxygen give, when ignited (or in the presence of a piece of spongy platinum), a

still more violent explosion. The energy with which oxygen and hydrogen unite is turned to practical account in the oxy-hydrogen blowpipe and in Deville's oxy-hydrogen furnace. These are amongst the most powerful sources of heat at our command. In the oxy-hydrogen blowpipe the two gases are not allowed to come in contact till just before they issue, mixed in the proper proportions. The flame, which is very feebly luminous, melts thin platinum wire with ease, causes iron or steel wire to burn with vivid scintillations, liquefies rock crystal, and, when made to impinge on a cylinder of lime, causes the lime to become white hot, and to emit light of great steadiness and intensity, known as the lime-light, or Drummond light, after its inventor, Lieut. Drummond. Hydrogen is not poisonous. With the aid of heat, hydrogen combines directly with several elements, especially with chlorine, the next element which must engage our attention.

CHLORINE, Cl_2.

Atomic Weight and Sp. Gr. = 35·5. *Molecular Weight* = 71. *Molecular Volume* $\square\square$. 1 *litre weighs* 35·5 *criths. Equivalence* 1.*

Occurrence. This element, the most important member of a class of elements known as the "halogens," was discovered by Scheele, in 1774. It constitutes rather more than 60 per cent. of sodic chloride (NaCl), or common salt, which occurs plentifully in beds in various parts of the world, and of which nearly 3 per cent. of sea water consists.

Preparation. This is practised on a very large scale in the manufacture of bleaching powder (the so-called "chloride of lime"). Hydrochloric acid and manganic oxide (or binoxide of manganese) are the materials used.

* The meanings of these terms and figures will be explained in Chapters V and VI.

On a small scale the gas is prepared by gently heating a quantity of manganic oxide with some rather concentrated solution of hydrochloric acid, in a flask or retort; chloride of manganese and free chlorine are thus produced:

$$\underset{\text{Manganic oxide.}}{MnO_2} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Manganous chloride.}}{MnCl_2} + \underset{\text{Water.}}{2OH_2} + Cl_2.$$

Instead of hydrochloric acid, common salt and sulphuric acid may be added to the manganic oxide with the following effect:—

$$\underset{\text{Manganic oxide.}}{MnO_2} + \underset{\text{Sodic chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{2SO_4H_2} = \underset{\text{Manganous sulphate.}}{SO_4Mn} + \underset{\text{Sodic sulphate.}}{SO_4Na_2} + \underset{\text{Water.}}{2OH_2} + Cl_2.$$

Some hydrochloric acid escapes with the chlorine, and may be removed by allowing the gas to bubble through a little water in a wash-bottle, as in the figure.

Chlorine should be collected either over warm water, in which it is not so soluble as in cold water, or by downwards displacement in dry bottles, to the bottom of which the delivery tube is allowed to reach. Owing to diffusion the latter method has these disadvantages, that the gas obtained is not free from air, and that a good deal of it escapes, and renders its presence in the atmosphere, even in very small quantities, very perceptible, by producing great irritation of the air-passages, attended with coughing. It cannot be collected over mercury (which is used instead of water for many soluble gases), because it acts on that metal with great rapidity.

Properties. Chlorine is a transparent, greenish-yellow gas, with a suffocating, irritating odour. It has the specific gravity 35·5, and is therefore about $2\frac{1}{2}$ times as heavy as atmospheric air. A pressure of 4 atmospheres at 15°·5 C. reduces it to a yellow, limpid liquid (sp. gr. 1·33) which remains unfrozen even at — 140° C. Cold water dissolves about twice its volume of chlorine; the solution has the colour, odour, and

astringent taste of the gas; even at 40° C. water dissolves 1·36 times its bulk of the gas.

Chlorine is not combustible in air or oxygen, nor will it combine directly with oxygen. But it has a great affinity for hydrogen, and will support the combustion of substances rich in hydrogen, such as an ignited wax taper, or a bit of paper dipped in oil of turpentine, which bursts into flame on being plunged into the gas. But chlorine will not, even at a high temperature, support the combustion of carbon, and the carbon of the taper and of the turpentine is deposited as dense black smoke. Phosphorus, powdered arsenic, antimony, or iron, copper leaf, sodium (previously warmed), &c., take fire spontaneously in chlorine, the product being in each case the chloride of the element. The following facts illustrate the intense affinity which exists between chlorine and hydrogen. These gases explode violently, forming hydrochloric acid, when mixed together in equal volumes, and exposed either to bright light (*e.g.*, that produced by burning a mixture of carbonic disulphide vapour with nitric oxide), or to heat, or to the electric spark. Free chlorine removes hydrogen from bodies which contain it, especially from organic compounds, substituting for each atom so withdrawn an atom of chlorine: for example—

$$\underset{\text{Marsh gas (methylic hydride).}}{CH_4} + Cl_2 = \underset{\text{Methylic chloride.}}{CH_3Cl} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

$$\underset{\text{Methylic chloride.}}{CH_3Cl} + 2Cl_2 = \underset{\text{Chloroform.}}{CHCl_3} + 2HCl.$$

Chlorine is, on these accounts, a powerful bleaching agent, decomposing the vegetable colouring matters which contain hydrogen, and forming instead colourless compounds containing chlorine. Chlorine permanently discharges the colour of ink, tincture of litmus, indigo, log-wood, turkey-red, &c. The presence of water is essential to these changes, *e.g.*:—

$$\underset{\text{Indigo.}}{C_8H_5NO} + \underset{\text{Water.}}{OH_2} + 2Cl_2 = \underset{\text{Chlorisatin.}}{C_8H_4ClNO_2} + \underset{\text{Hydrochloric acid.}}{3HCl}.$$

To the same property are due the valuable and potent disinfecting and deodorising effects of chlorine, as well as its irritating and virulently poisonous action on the mucous membrane of the human air-passages and lungs.

Chlorine is capable of uniting directly or indirectly with every other element with which we are acquainted.

Uses. Chlorine is largely used, either free, in solution, or in combination with oxygen and the metal calcium as bleaching powder ($CaOCl_2$), for bleaching linen and cotton goods, rags for the manufacture of paper, &c., and for disinfecting purposes. In the laboratory it is useful as an oxidising agent. Owing to its attraction for hydrogen and basylous elements and radicals, it decomposes water and bases, liberating oxygen, which, in this *nascent* condition, readily enters into new combinations. This is exemplified by the formation of chlorisatin in the action of chlorine-water on indigo above explained; also chlorine-water, exposed to sunlight, gives the following substitution:—

$$2OH_2 + 2Cl_2 = 4HCl + O_2.$$

COMPOUND OF HYDROGEN WITH CHLORINE.

Hydrogen and chlorine cannot, either directly or indirectly, be made to unite to form more than one compound, viz.:—

HYDROCHLORIC ACID.

Molecular Weight = 36·5. *Molecular Volume* □□. 1 *litre weighs* 18·25 *criths.* *Sp. Gr.* 18·25.

This very important compound has also received the following names: spirit of salt, marine acid, muriatic acid chlorhydric acid, and hydric chloride.

It is evolved in large quantities from volcanoes, and was discovered in 1772 by Priestley.

Preparation. 1. Place some fragments of fused sodic chloride (common salt) in a retort or flask such as was used in preparing chlorine, add some dilute sulphuric acid, and apply a gentle heat.

$$\underset{\text{Sodic chloride.}}{NaCl} + \underset{\text{Sulphuric acid.}}{SO_4H_2} = \underset{\text{Hydric sodic sulphate.}}{SO_4HNa} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

The gas evolved should be collected over mercury, unless only a solution of the gas be required, when it is conducted into a series of Woulfe's bottles partly filled with water. In the first of these all impurities are arrested; in the second (which should be kept cool by immersion in water, on account of the heat with which the absorption of the gas is accompanied) the solution of most of the hydrochloric acid is formed; and the rest of the acid is taken into solution in the remaining bottles.

This method is also employed on the large scale, iron cylinders being substituted for a flask, and stoneware jars for wash-bottles.

2. This gas may be obtained by the direct combination of its constituent elements, as above described (p. 46).

Properties. Hydrochloric acid is a transparent, colourless gas, with a pungent odour, intensely acid taste, and irritating effect on the eyes. Though far less offensive in its action on the air-passages and in its odour than chlorine, it produces coughing even when largely diluted with air. Its specific gravity is 18·25, for when equal volumes of hydrogen and chlorine combine no alteration of volume takes place, and the specific gravity of the resulting compound is consequently the mean of the specific gravities of its constituents. This fact may be represented by the following diagram:—

$$\boxed{1} + \boxed{35{\cdot}5} = \boxed{18{\cdot}25}\boxed{18{\cdot}25}$$

Under a pressure of 40 atmospheres at 10° C. this gas is condensed to a colourless liquid (sp. gr. 1·27), which has never been frozen. Water absorbs pure hydrochloric acid gas instantaneously. If a jar of the gas be opened under water, the water rushes in, filling the jar with almost explosive violence. A lump of ice in an atmosphere of hydrochloric acid absorbs the gas and liquefies rapidly. At 15° C. water absorbs 458 times its bulk, or nearly its own weight of the gas, increasing in volume one-third, and acquiring a specific gravity of 1·21. The properties of the solution are given below.

Hydrochloric acid is not combustible, nor will it support combustion. A piece of potassium heated to redness in this gas burns, leaving only the hydrogen, which is found to occupy half the original volume:

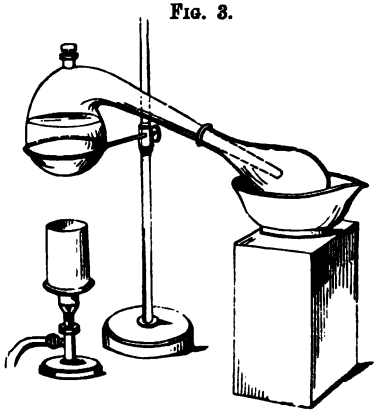
$$K_2 + 2HCl = \underset{\text{Potassic chloride.}}{2KCl} + H_2.$$

Hydrochloric acid reddens dry litmus paper. When in contact with air containing moisture, it produces white fumes. It may be partly decomposed into its constituents by passing electric sparks through it.

Solution of Hydrochloric Acid. When it has the density 1·21, the liquid is fuming and colourless, and, on a slight elevation of temperature, parts with the gas abundantly. When subjected to distillation it loses hydrochloric acid till the liquid has a spec. grav. of 1·1; it then distils over at 106° C. unchanged. Distillations of this kind are effected by means of such an apparatus as that represented in Fig. 3. A weaker acid loses water when heated, till its spec. gravity is as high as 1·1, and then it distils over at 106° C. without change. A solution containing a larger percentage of hydrochloric acid, and having, in consequence, a higher specific gravity, will distil over without change under a greater atmospheric pressure. Hydrochloric acid in solution is decomposed by the electric current; hydrogen is liberated at the negative, chlorine at the positive, pole or electrode of the

battery; most of the chlorine so evolved is taken into solution. Hydrochloric acid, whether free or in solution, may

FIG. 3.



be decomposed, with separation of hydrogen, by many metals —by potassium, for instance (v. sup.). All the metals which at a red heat decompose water will resolve hydrochloric acid in solution into its constituents; *e.g.*, zinc forms with the acid zincic chloride and free hydrogen,

$$Zn + 2HCl = \underset{\text{Zincic chloride.}}{ZnCl_2} + H_2.$$

The action of the metal on this acid is quite similar to its behaviour with sulphuric acid already described (p. 38), and hydrogen may, in fact, be prepared by this process. The action of hydrochloric acid on the hydrates and oxides of the metals is exemplified by the following equations :—

$$\underset{\text{Potassic hydrate.}}{OKH} + HCl = \underset{\text{Potassic chloride.}}{KCl} + OH_2.$$

$$\underset{\text{Zincic oxide.}}{ZnO} + 2HCl = \underset{\text{Zincic chloride.}}{ZnCl_2} + OH_2.$$

Common Impurities of the Commercial Acid. Iron, which turns the solution yellow, sodic chloride, arsenious chloride (from impure sulphuric acid used by the manufacturer), sulphuric and sulphurous acids, and chlorine. Of these, the two first may be removed by diluting the acid till its specific gravity is 1·1, and then distilling. The following tests may be applied to small portions of the dilute acid to ascertain whether the most important impurities are present :—

Sulphuric acid gives, with baric chloride, a white precipitate; the presence of arsenic is revealed by a yellow precipitate with sulphuretted hydrogen; whilst, in the presence of iron, potassic ferrocyanide gives a precipitate of Prussian blue.

*Test for Hydrochloric Acid.** A solution containing even a mere trace of the acid, or of a chloride, gives, on the addition of a drop of argentic nitrate, a white, curdy precipitate of argentic chloride, soluble in ammonia, but insoluble even in hot nitric acid. The following is the reaction :—

$$\underset{\text{Sodic chloride.}}{NaCl} + \underset{\text{Argentic nitrate.}}{NO_3Ag} = \underset{\text{Argentic chloride.}}{AgCl} + \underset{\text{Sodic nitrate.}}{NO_3Na}.$$

Uses. Hydrochloric acid is principally employed in the manufacture of bleaching powder, but also in the preparation of potassic chlorate and sal-ammoniac. It is used as a solvent for tin by the dyer and calico-printer.

* The tests mentioned in this book must be regarded as distinguishing the substance in question from *most* other substances but not necessarily from all.

Chapter V.

ATOMIC WEIGHTS AND VOLUMES.

A knowledge of the facts concerning hydrogen, chlorine, and hydrochloric acid contained in the last chapter enables us now to enter upon the study of some of the laws which govern the chemical force. An early acquaintance with the broad foundations of the science, as a preliminary to the study of its minute details, is highly desirable, as it will materially assist the beginner in rightly understanding and comparing the varied phenomena brought under his observation, whilst facts which might otherwise be dry and burdensome to the memory may thus be invested with new interest and significance.

Atomic Weights.—We have seen that hydrogen and chlorine combine in fixed proportions and form but one compound. And we have called the numbers expressing the proportions by weight in which they unite—viz. 1 and 35·5—their atomic weights.

Combining Proportions. But there are pairs of elements which form more than one compound with each other,—which, though the proportions that go to form each compound are fixed and invariable, combine in more proportions than one. Mercury forms with chlorine two compounds, popularly known as calomel and corrosive sublimate. Nitrogen and oxygen combine with each other in five different proportions to form five distinct compounds. The proportion by weight of nitrogen to oxygen in each is expressed in the simplest form by the following ratios:

7 : 4 , 7 : 8 , 7 · 12 , 7 : 16 , 7 : 20.

A glance at these ratios is sufficient to produce the conviction that nitrogen does not invariably combine only with one atom, or some one number of atoms, of oxygen, but that it combines with different numbers of atoms of oxygen. If we were acquainted with only one of these compounds, we might be led to the erroneous supposition that it was built up like hydrochloric acid, that in its molecule but one atom of each element was present. We might further suppose that the numbers expressing the relative weights of nitrogen and oxygen expressed also their atomic weights; but we shall learn by-and-by that, unless the compound which we chanced to possess happened to be that in which the ratio of nitrogen to oxygen is as 7 to 8, and unless we were to put down the relative weights as 14 and 16, we should not have hit upon the numbers truly representing the atomic weights of nitrogen and oxygen when that of hydrogen is taken as unity.

Moreover there are pairs of elements which resemble hydrogen and chlorine in combining with one another to form but one compound, and yet differ from those elements in the fact that the compound molecule produced does not consist of *one* atom of the one element united with *one* atom of the other. For example, the ratio 14 to 3 is that in which nitrogen and hydrogen combine We should, however, be in error if on this account we declared that 14 and 3 are respectively the atomic weights of nitrogen and hydrogen: and if, having decided to call the atomic weight of hydrogen unity, we were to fix that of nitrogen at $\frac{14}{3}$ or 4·66, we should be equally mistaken. The truth is that with one atom of nitrogen as many as three atoms of hydrogen are combined; and, therefore, the atomic weight of nitrogen is 14.

Hence arises the question—how are we, from the apparently conflicting evidence of different compounds, to determine what are the atomic weights of their component elements? How are we to decide whether a given molecule contains only one atom, or more than one atom of each of its constituents?

The magnitude of the difficulties which have beset these enquiries may be gathered from the fact that within a very few years a necessity has been discovered for altering a large proportion of the atomic weights which it had been customary to assign to the elements: those of carbon, oxygen, sulphur, selenium, and tellurium were in the first place* doubled by Berzelius†: that of Silicon has been altered from 21 to 28·5: whilst those of more than half the metals have more recently been doubled in compliance with the suggestions of M. Cannizarro and M. Wurtz. It is not at all certain that further advances of our knowledge may not necessitate fresh modifications of a similar nature, although chemists have now been enabled by certain important considerations—physical as well as chemical—to decide with some approach to certainty what is the number which represents the atomic weight of each element most truly.

These chemical and physical requirements, in accordance with which the numbers are selected, are as follows:—

i. *Chemical.* (1.) The numbers must correspond with the proportions by weight in which the elements are found to exist in compounds, and to combine with other elements.

(2.) They must illustrate analogies between similar bodies.

(3.) The numbers chosen must be such that the entire series of combinations of each element are expressed by a simple series of formulæ.

ii. *Physical.* (1.) Numbers should be selected according, as completely as may be, with Ampère's Law of Volumes (see next page).

(2.) They should fall, as far as possible, within the law already enunciated (p. 32), which declares that "the product

* This change was in accordance with a suggestion made by Sir Humphrey Davy, and resisted by Dalton and other eminent chemists, and more recently revived by Laurent and Gerhardt.

† Berzelius also doubled those of many other elements the old atomic weights of which were subsequently restored—some rightly, but most of them wrongly—by Gerhardt.

of the specific heat and atomic weight is almost invariably a sensibly constant quantity."

(3.) They must, as a rule, give similar formulæ to isomorphous compounds, that is, to substances which crystallise in the same forms (ἴσος, equal; μορφή, shape).

"Now it so happens that these different requirements, chemical and physical, are not always satisfied by one and the same number. Hence we have to subordinate requirements, much in the same manner that zoologists and botanists subordinate characters, and to select that atomic weight which fulfils the greatest number, or rather the most important of them. Many of the discrepancies which were formerly thought to exist between the numbers deduced respectively from chemical and physical considerations have of late years been satisfactorily explained away; and we have every reason to believe that, with increasing knowledge leading to higher generalisations, all such anomalies as at present exist will also disappear."* It is by this accumulation, comparison, and weighing of evidence that the atomic weights given in the table at p. 10 have been determined.

Atomic Volumes.—Before proceeding further in this subject, we must give our attention to the first of the physical requirements which govern the selection of atomic weights; for it is from the observation of the *combining volumes* of gases and vapours that we derive the most important of all means for controlling our conclusions.

Ampère's Law of Vapour Volumes. When either the element in question or one of its compounds is volatile or gaseous, the most valuable evidence of its atomic constitution is afforded by the remarkable law, the earliest conception of which is attributable to Gay-Lussac, though it was first clearly enunciated by Ampère, namely: *that all gases and vapours contain the same number of molecules within the same volume;* a

* Watts's Dict. of Chemistry; article on Atomic Weights, by Dr. Odling.

law which may also be expressed as follows:—All molecules in the state of gas or vapour occupy the same volume at the same temperature and barometric pressure; in other words, at the same temperature all molecules offer an equal amount of resistance to the atmospheric pressure. In the molecules of *compounds*, according to the atomic weights which we have adopted, there are but very few exceptions to this beautiful law. And, if we assume that the molecules of elementary bodies ordinarily consist of two atoms—and we shall hereafter see that there are the best reasons for entertaining this view—the law holds true also with regard to such *elements* as we have hitherto succeeded in obtaining in the gaseous or vapourous condition;* that is to say, the atoms of elements occupy the same volume in the state of gas or vapour, or half the volume which is occupied by their molecules; and the specific gravities of elementary gases and vapours, when that of hydrogen is taken as unity, are consequently expressed by the same numbers which express their atomic weights: for instance, since the atomic weights of hydrogen and chlorine are 1 and 35·5, and since an atom of hydrogen occupies the same volume as an atom of chlorine which weighs 35·5 times as much—if the specific gravity of hydrogen is 1, that of chlorine is 35·5. And further, a molecule of hydrogen exploded with a molecule of chlorine would give two molecules of hydrochloric acid, which occupy the same volume as the two original elementary molecules.

If any instance should arise in which it is found that the volume occupied by the supposed atom—the *combining* or *atomic volume*—of an element, the atomic weight of which has been deduced from chemical considerations, does not accord with this law, then there will be—as there has been in the cases cited above (p. 54)—a necessity for debating whether the assumed atomic weight of the element must not be changed, so

* Five apparent exceptions to this rule in the cases of phosphorus, zinc, cadmium, mercury, and arsenic, have as yet received only hypothetical explanations.

that its atom and its molecule may be declared to occupy their normal volumes. Or, if the volumes of the assumed molecules of its compounds should be abnormal, the question will present itself whether the atomic weight of the element should not be so determined, that this apparent exception to the law may be removed.

Standard Volume. For the practical application and experimental verification of this wonderful and simple "Law of Vapour Volumes," it is necessary that we should fix on a standard volume, so that the weights of the same volumes of different bodies, simple and compound, may be readily compared. Unfortunately two different standard volumes have been proposed. Each is extensively employed, and should, with the weight of hydrogen which it represents, be carefully committed to memory by the student.

The first of these standards, namely that proposed by Dr. Hofmann, and called by him his "volume-weight-unit," is as follows:—The unit of volume is 1 cub. decimetre (= 1 litre) at 0° C. and 760 mm. bar. pressure. The weight of 1 litre of hydrogen (at 0° C. and 760 mm.) is 0·08961 grm., and is called 1 *crith* (κριθή, a barley-corn). Hence the weights of 1 litre of chlorine, oxygen, and nitrogen are respectively 35·5, 16, and 14 criths; and that of 1 litre of hydrochloric acid, the specific gravity of which is 18·25, is 18·25 criths.

The other standard is that employed by Dr. Williamson: the volume occupied by one gramme of hydrogen (at 0° C. and 760 mm.), or 11·15947 litres. 35·5 grms. of chlorine, 16 grms. of oxygen, 14 grms. of nitrogen, and 18·25 grms. of hydrochloric acid all occupy just 11·15947 litres at 0° C. and the normal barometric pressure.

Chapter VI.

EQUIVALENCE, OR ATOMICITY, AND NOTATION.

Equivalence.—Having now come to a complete agreement as to the manner in which its true atomic weight is to be assigned to each element, we must in the next place apply ourselves to the consideration—and if possible to the explanation—of the fact that some elements never combine with each other in that simple proportion in which alone, on the other hand, other elements like hydrogen and chlorine combine,—whilst some combine with each other in more proportions than one.

Typical Compounds. The formula HCl represents the only compound formed by the union of hydrogen with chlorine:

The chief compound of hydrogen with oxygen is represented by OH_2:

The only compound of hydrogen and nitrogen is NH_3:

The commonest compound of hydrogen with carbon has the formula CH_4.

Thus we see that the oxygen atom has the power of combining with twice as much, the nitrogen atom with three times as much, and the carbon atom with four times as much hydrogen as the chlorine atom.

Again, whilst the hydrogen atom combines with only one atom of chlorine, we observe that the magnesium atom can combine with two, the bismuth atom with three, the tin atom with four, and the antimony atom with as many as five atoms of chlorine,—these compounds being severally represented by the formulæ $MgCl_2$, $BiCl_3$, $SnCl_4$, and $SbCl_5$.

We thus find that an atom of oxygen is capable of re-

placing—is in fact *equivalent* to—two atoms of chlorine, an atom of nitrogen is equivalent to three, and an atom of carbon to four atoms of chlorine, an atom of magnesium to two atoms of hydrogen, and so on; and we are led to the conviction that the *equivalents* of elements are not necessarily their atomic weights. The *equivalence* of an atom—that is the number of atoms of hydrogen (the unit of equivalence as well as of specific gravity and atomic weight) to which its atom is equivalent—is generally expressed in Roman figures, i, ii, iii, iv, &c. Many chemists still prefer to employ the term *atomicity*, which, in its modern restricted sense, is exactly synonymous with *equivalence*.

Monads. Now there are several elements which, like hydrogen, combine with only one atom of chlorine,—or, like chlorine, with only one atom of hydrogen; amongst these are sodium, potassium, silver, bromine, fluorine, and iodine; and they form such compounds as the following:—

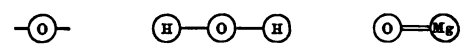
NaCl, KCl, AgCl, HBr, HI, &c.

All these elements are distinguished as "*monads*," and are said to be "*monequivalent*." We never find an atom of any of these elements forming a compound with more than one atom of any single other element. This fact may be roughly rendered intelligible to the mind by representing the atom graphically as a ball, in which is fixed a single rod or peg—a bond of connection—by means of which it may become attached to another atom possessing a similar bond:—

But it has not a second bond or unit of chemical affinity by which it could attach to itself a second atom. The molecule HCl may be represented graphically thus:—

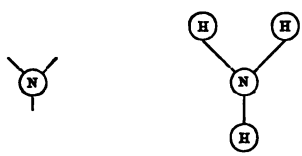
Diads. Elements like oxygen and magnesium, the atoms

of which unite with two atoms of these monads, are called "*diads*," and are distinguished as "*diequivalent*." The following are graphic formulæ for a diequivalent atom, for the molecule of water, and for the molecule of magnesia, in which one diequivalent atom is combined with another :—

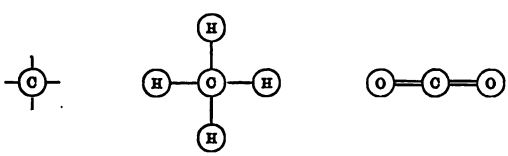


The same idea which the bonds convey in a graphic formula may also be expressed with the ordinary symbols by means of accents, or "*equivalence-marks*." The symbols of diequivalent elements should, for instance, except where it is very obvious what must be the equivalence of the atom, be accented thus : Mg″, O″, S″, &c.

Triads. Nitrogen, bismuth, &c. (N‴, Bi‴, &c.), may be called "*triads*," or "*triequivalent*" elements. The graphic formula for triequivalent nitrogen, with that for the molecule NH_3, is given below :—

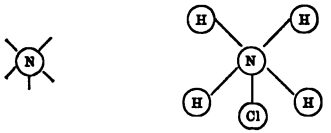


Tetrads. Carbon, tin, &c. (C^{iv}, Sn^{iv}, &c.) are "*tetrads*," or "*tetrequivalent*" elements. The following are representations of a tetrequivalent atom, and of the molecules CH_4 and CO_2:—

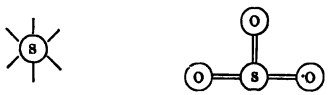


Pentads. Many triads, nitrogen for example, may also be "*pentads*" or "*pentequivalent*" at times. Their atoms have then to be represented as having five bonds or units of force.

The equivalence-mark v is attached to their symbols, and their compounds have to be explained by such graphic formulæ as that here given for the molecule $N^{v}H_4Cl$:—



Hexads. Diads can frequently also exert, under favourable circumstances, tetrequivalent, or even "*hexequivalent*" powers. Sulphur, for instance, is frequently a "*hexad*," as, for example, in the molecule $S^{vi}0''_3$:—



Thus we see that the equivalence of the same element may apparently, under differing circumstances, vary. It remains to be declared as a law to which no exceptions—but such as admit of a simple explanation, and are, therefore, more apparent than real—exist, that an element having an even equivalence cannot ever become odd-equivalent, and that an element which has an odd equivalence can never possess an even equivalence. In this way the elements can be divided into two perfectly well-defined classes of odd-equivalent and even-equivalent elements, of "*perissads*" and "*artiads*," * or "*perissequivalent*" and "*artiequivalent*" elements.

Thus it appears to be a law which it is not possible to challenge that, if the equivalence of an element varies, the number expressing the equivalence never varies otherwise than by the addition or subtraction of an even number.

Dr. Frankland has recently suggested that this fact is to be accounted for by assuming that, when, for instance, an

* These two names have been proposed by Dr. Odling (περισσός, uneven, odd; ἄρτιος, even).

element which is sometimes pentequivalent exerts only triequivalent attractions, two out of the five bonds which go to make up the equivalence of its atom unite with and satisfy each other. Sulphur may be regarded as invariably in truth hexequivalent. When it appears to be only tetrequivalent, a pair of the six bonds may be satisfying each other; and when it seems to be a diad, two pairs of these bonds are perhaps thus engaged. The atoms of triequivalent and monequivalent nitrogen, tetrequivalent sulphur, and diequivalent sulphur, ought, if these views be correct, to be graphically represented as follows:—

In adopting this hypothesis, Dr. Frankland distinguishes the maximum number of bonds of an element as its *absolute equivalence*, the number of bonds united together as its *latent equivalence*, and the number of bonds or units of chemical force actually engaged in linking it with the other elements of a compound as its *active equivalence*.

In a vast number of compounds we shall find that two or more atoms of the same element are chemically connected by one or more bonds of each: we shall presently have to observe also that the molecules of most elements consist of two atoms held together by all the bonds of each; the only question, if it can still be called a question, is whether bonds belonging to the same atom ever unite together.

Compound Radicals. Two important conclusions may now be deduced from the facts to which the study of the subject of *equivalence* has introduced us:—

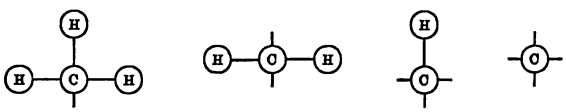
i. Molecules are always so bound together by the bonds which constitute the equivalences of their component atoms, that none of these bonds are disengaged or unsatisfied, and consequently the sum of the bonds is always an even number.

Hence, no molecule is correctly represented by any formula

according to which the total number of units of chemical affinity of the component atoms is uneven; or no molecule can contain an odd number of perissequivalent atoms.

ii. No portion of a molecule can be removed without leaving one or more of the bonds of the atoms of the molecule unsatisfied, the substance left being consequently incapable of a separate existence.*

For instance, $C^{iv}H_4$ is a molecule; take away an atom of H, and you leave $C^{iv}H_3$ which has a bond unsatisfied; take away H_2, and you have $C^{iv}H_2$ which has two bonds unsatisfied; take away H_3, and you leave $C^{iv}H$, which has three bonds uncombined; take away H_4, and you leave C^{iv}, which has four bonds unoccupied, and is consequently called a tetrequivalent elementary atom, or a tetrequivalent *simple radical.* All these residues are shown in the following graphic formulæ :—



Now it is evident that, just as an atom of carbon is, by virtue of having four free bonds, a tetrequivalent *simple radical*, so the residues CH_3, CH_2, and CH may respectively, according to the number of unoccupied bonds they possess, be called monequivalent, diequivalent, or triequivalent *compound radicals;* for their unsatisfied or unsaturated condition renders

* There are some cases in which, the number of unsatisfied bonds being even, they are capable of uniting with each other so that the residue is able to exist as a molecule, *e.g.* $C^{iv}O_2 - C = O_2$.

$$C^{iv}O_2 - O = {}''C''O.$$

$$C^{iv}OCl_2 - Cl_2 = {}''C''O.$$

And in some instances a re-arrangement of the atoms takes place in the residue :

$$\left\{\begin{matrix}'O'H\\'O'H\end{matrix}\right. - O_2 = H_2; \qquad Ba''(OH)'_2 - OH_2 = Ba''O;$$

$$S^{vi}O_2(OH)'_2 - OH_2 = S^{vi}O_3.$$

them capable of acting like simple radicals or elements, which they can even displace in compounds. The equivalence of a compound radical is i, ii, iii, or more, according to the number of monad atoms necessary to convert it into a complete molecule.

It is frequently convenient to give names to compound radicals, and to substitute for the formula expressing their composition a single symbol. Thus, for example, the radical $C^{IV}H_3$ is called methyl, and is usually represented by the symbol Me; and the radical O″H —(O)—(H) (which is evidently monequivalent) is called hydroxyl, and has the symbol Ho; NaO receives the name Sodoxyl, and the symbol NaO; whilst the names and symbols of Zn″O_2—(O)—(Zn)—(O)—, Cu″O_2, &c., (which are diequivalent radicals) are zincoxyl —Zno″, cuproxyl —Cuo″, &c. (See p. 103.)

NOTATION.—On account of the great significance and importance of the foregoing laws, and the bearing that they have on the chemical properties and relations of elements and compounds, it is exceedingly desirable that the forms in which chemical formulæ are, for most purposes, written should be such that it may be readily apparent how each unit of force of the several atoms is expended.

Graphic and Symbolic Formulæ. Graphic notation in the form invented by Dr. Crum Brown,* effects this object most completely and satisfactorily. Coloured balls connected together by brass rods, forming the "glyptic" formulæ first devised by Dr. Hofmann,† represent graphic formulæ admirably in the lecture room. But even symbols may be so dis-

* Dr. Crum Brown's system of graphic notation, which has been adopted for teaching purposes by Dr. Frankland and other chemists, seems not to be open to the objections which have been satisfactorily made out against that on the same principle previously proposed by Professor Kekulé.

† A box of balls and rods and india-rubber connections, well adapted to a lecturer's wants, may be obtained of Mr. Blakeman, of Gray's Inn Road. The term "glyptic" has been coined from γλυπτός, carved.

posed as to enable the written formula for a molecule to explain, almost as clearly as these more elaborate devices, in what manner, and between which elements, the units of affinity of its constituents are mutually engaged.

Rules of Symbolic Notation. The rules which we shall follow in the more complicated formulæ, when we wish to bring out the internal structure of a molecule, are these:—We shall place first (on the left) the symbol of an element the available bonds of which are directly united with all the available bonds of the other elements or radicals whose symbols follow upon the same line. This first symbol, unless the element be a monad, will be printed in thick type, and will usually represent the most polyequivalent element (*i.e.*, the element having the highest equivalence) in the compound. According to this rule, we should write the equation on p. 39 as follows:—

$$\mathbf{S}^{vi}O_2Ho_2 + Zn = \mathbf{S}^{vi}O_2Zno'' + H_2.$$

By the expression the "available bonds" is meant, with respect to the elements and radicals following the symbol in thick type, those bonds which do not unite these elements and radicals to each other;—whilst, with respect to the atom occupying the prominent place in thick type, is meant that part of its active equivalence which is not engaged in uniting it to another atom the symbol of which is placed perpendicularly above or below it in the formula. When any bonds of these central or governing atoms are thus engaged, a bracket is used to connect the lines of the formula together, and to express this combination. Thus:—

$$\left\{\begin{matrix}'\mathbf{Fe}'''Cl_3 \\ '\mathbf{Fe}'''Cl_3\end{matrix}\right.$$

The structure of a compound of this kind may be represented in one line by such a formula as the following:—

$$'\mathbf{Fe}'''_2Cl_6.$$

When there is no difficulty which might cause hesitation as to the equivalence to be ascribed to any of the atoms, and when the manner in which all the bonds are satisfied is immediately evident, it will not be necessary to insert the equivalence marks. They will be omitted in the cases of monads, of oxygen, which appears invariably to be a diad, and of carbon, except where the active equivalence of this element is reduced to ii.

Atomic and Molecular Equations. It may be inferred from our conclusions respecting the constitution of *molecules* (p. 62), that the molecules of perissad elements cannot consist of less than two atoms. The general law that the molecules of elements consist of two atoms is extended by the consideration of their vapour-volumes to many artiads also; but it is doubtful whether the molecules of some at least of the diequivalent metals do not coincide with their atoms. In these exceptional instances the two bonds of the atom seem to be satisfying each other.

For these reasons, in representing reactions, decompositions, &c., it is not customary to use equations like the following, which may be called an "*atomic equation*" (except where the atom is presumed to be identical with the molecule, *e.g.*, in the case of zinc):—

$$\mathbf{O}H_2 = H_2 + O,$$

but, because the atom O cannot exist in the free state, "*molecular equations*," which represent much more correctly what takes place, are preferred:—

$$2\mathbf{O}H_2 = 2H_2 + O_2.$$

We shall presently have to notice some elementary substances, "allotropic" modifications of elements, whose molecules undoubtedly consist of more than two atoms of the same element (v. p. 81). The molecules of phosphorus and a few other elements probably consist of four atoms.

Chapter VII.

CLASSIFICATION OF ELEMENTS AND NOMENCLATURE.

Before we resume the study of the elements it will, in the first place, be well to form a definite plan of the order we must pursue—the classification of our subject which we must adopt—in order to consider their relations to each other, and the similarities of their compounds, to the best advantage; and, in the second place, we must devote a few pages to developing such a system of nomenclature as will enable us clearly to express in words the constitution of compound substances.

Classification of the Elements.—The following table shows at a glance into what groups those elements with which we have to deal in this volume most naturally divide themselves. The sharp distinction, first of all, between perissads and artiads, according as the element's equivalence is odd or even, furnishes two great classes, the first of which may again be divided so that one of the sub-classes includes all the monads, whilst the second comprises the triads and pentads. The members of each of these three groups further arrange themselves naturally, according to certain similarities and differences in chemical properties, in two sections; finally they may be sorted into two distinct columns according as their constituent elements are *chlorous* or *basylous*.

Hydrogen, chlorine, oxygen, nitrogen, and carbon, the representatives of the most important sections, and the compounds of these elements with each other, demand an earlier and a more careful and detailed examination than the remain-

ing elements and compounds. Hydrogen and chlorine have already come under our notice: we shall, in the next place, therefore, proceed to the study of oxygen, nitrogen, and carbon, and of their compounds with hydrogen.

Perissads.			Artiads.	
Monads.		Triads and Pentads.	Diads, Tetrads, and Hexads.	
Basylous.	Chlorous.	Basylous.	Chlorous.	Basylous.
Sect. 1.	Sect. 2*.	Sect. 1.	Sect. 1.	Sect. 2.
H = 1	F = 19	B‴ = 11	O″ = 16	C^{iv} = 12
	Cl = 35·5		S^{vi} = 32	Si^{iv} = 28·5
	Br = 80	Sect. 2.	Se^{vi} = 79	Ti^{iv} = 50
	I = 127	N^{v} = 14	Te^{vi} = 129	Sn^{iv} = 118
		P^{v} = 31		
		As^{v} = 75		
		Sb^{v} = 122		
		Bi^{v} = 208		

As the names of the elements can be readily found by referring to the table at p. 10, their symbols and atomic weights alone are given here. The equivalence-marks indicate what is the highest equivalence each element is known to be capable of possessing.

The following quotation from Dr. Odling's Chemistry will explain the distinction made in the classification between *basylous* and *chlorous* elements:—

"It is found, as a general rule, that elements which have the strongest tendencies to combine with one another are possessed of opposite properties. The metals potassium and sodium, and their congeners, which constitute the basylous

* It is not improbable that the members of this section are really triads, though their active equivalence is seldom more than i. Iodine seems in some organic compounds to possess triequivalent affinities.

class of elements, are characterised in the highest degree by one set of properties; while chlorine and the bodies more or less closely allied to it, which constitute the chlorous or acidulous class, are characterised by an opposite set.

"Under certain conditions, very many chemical compounds are decomposed when traversed by the electric current. As a result of this electrolytic decomposition, the basylous elements are liberated at the negative pole, and are thence termed electro-positive, as an inference from the well-known law that oppositely electrified bodies attract one another; while the chlorous elements are liberated at the positive pole, and are thence termed electro-negative. But chlorous, or electro-negative, and basylous, or electro-positive, elements are not separated from one another by any peculiar distinctive character, they are but as links, at either end of a long chain, and approximate to one another by insensible gradations. An element is negative to those on one side of it, positive to those on the other. Thus even sulphur, which is essentially chlorous in its habitudes, is nevertheless positive in respect to oxygen, and is liberated from its oxide at the negative pole."*

The eight chlorous elements enumerated above are electro-negative or chlorous to the remaining fifty-four elements which are more or less positive or basylous.

This distinction applies also to compound radicals; like elements, they may be basylous or chlorous.

NOMENCLATURE.—The advances made in the science of chemistry, since a system of nomenclature was first proposed, have necessitated such a vast addition to the number of names which any complete system must comprehend, and so many alterations of names already given, that it is difficult to restore to chemical nomenclature the simplicity essential to its usefulness. Nevertheless, the attainment to this desirable object has recently been attempted with considerable success. The only serious objection urged against the proposed changes is

* Dr. Odling's Manual of Chemistry, part I, p. 1.

the want of euphony in many of the new names of compounds. The force of this objection cannot be denied; it does not, however, seem sufficiently important to demand the rejection of a system the advantages of which will more than compensate the student for the loss of some old, irregular, but more euphonious names.

In sketching the outlines of the system only so far as is absolutely necessary for our purposes, I have the advantage of Dr. Frankland's permission to avail myself freely of the chapter on Nomenclature in his "Lecture Notes for Chemical Students."

The chemical name of a compound substance has two functions to perform.

The first is a function which must be performed by the names of elements also, and is common to all names whether scientific or not; the name must identify and individualise the substance. This end is readily attained even by such names as *salt*, *nitre*, &c.

Secondly, the name must express the composition (qualitative and quantitative)—the constitution—of the body to which it is applied. This is a condition which such names as *salt* and *nitre* do not satisfy, and which has been fulfilled to a most limited extent by the old scientific names formerly given to chemical compounds.

The Elements have received names which are absolutely arbitrary, but which frequently recall some of their most striking properties, *e.g.*, chlorine from χλωρός, greenish-yellow. Their names have not been formed according to any rule, except that those ending in *um* (except selenium) belong to *metals*, that those ending in *ine* are the names of a distinct group of *chlorous non-metals*, that those with the termination *on* belong to three elements which have long been classified together, whilst those which end in *gen* are the names of the three permanent* elementary gases.

* A permanent gas is one which has never been liquefied.

Compounds. A *binary compound* is the simplest kind of chemical compound, and is formed by the union of two elements. The names of these compounds are formed from those of their constituents, thus:—To the name of the basylous constituent, or to some abbreviation of either its English or Latin name, the terminal *ic* is added; and after it is placed a derivative of the name of the chlorous constituent made to terminate in *ide* (v. p. 75), thus:—

Potassium and sulphur, form potassic sulphide.
Silver and chlorine, ,, argentic chloride.
Zinc and oxygen, ,, zincic oxide.

To this rule, which enables a chemist to know the qualitative composition of a body, on simply looking at its name, some provision must be added for the purpose of rendering evident also its quantitative composition,—for the same elements frequently form with each other two compounds. In such cases, that compound which contains the smaller proportion of the chlorous element is often distinguished by the substitution of *ous* for *ic* in the terminal syllable of the first part of its name; and the terminal *ic* is reserved for the compound containing the larger proportion of the chlorous element (v. p. 75). The following example illustrates this rule:—

Stannous chloride, $\mathbf{Sn}''Cl_2$; Stannic chloride, $\mathbf{Sn}^{iv}Cl_4$.

In less frequent cases where elements form with each other more than two compounds, the distinctive prefixes *hypo* and *per* are frequently used, *e.g.*,

Plumbic peroxide, $\mathbf{Pb}^{iv}O_2$.

Or, in other cases, numeral prefixes are attached to each part of the name, so as to indicate how many atoms of each element are present in the molecule; for instance, a third oxide of tin is distinguished from stannous oxide and stannic oxide ($\mathbf{Sn}''O$ and $\mathbf{Sn}^{iv}O_2$) by the name

Distannic trioxide $\left\{ \begin{matrix} '\mathbf{Sn}'''O \\ '\mathbf{Sn}'''O \end{matrix} \right\} O$.

Oxides which form acids when they combine with water, or salts when added to bases, are generally characterised as *anhydrous acids* or *anhydrides*. The following are examples of anhydrides:—

Sulphurous anhydride, $S^{IV}O_2$. Sulphuric anhydride, $S^{VI}O_3$.
Nitrous anhydride, N'''_2O_3. Nitric anhydride, $N^{V}_2O_5$.

In several cases, of which the following are examples, the trivial or irregular names of binary compounds have not been replaced by the systematic names:—

Systematic Name.	Trivial or Irregular Name.
Hydric oxide.	Water.
Hydric sulphide.	Sulphuretted hydrogen.
Hydric chloride.	Hydrochloric acid.
Hydric carbide.	Marsh-gas or light carburetted hydrogen.
Hydric nitride.	Ammonia.

An acid may be defined as a compound containing one or more atoms of hydrogen, which it can exchange for potassium or sodium, when one of these metals is presented to it in the form of a hydrate. An acid containing one such atom of hydrogen is said to be *monobasic*, two such atoms *dibasic*, &c. Acids of a greater basicity than unity may be styled *polybasic*. The formation of water is always one of the results of this replacement of the hydrogen:—

$$\underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Sodic hydrate.}}{ONaH} = \underset{\text{Sodic chloride.}}{NaCl} + \underset{\text{Water.}}{OH_2}$$

$$\underset{\text{Sulphuric acid.}}{S^{VI}O_2Ho_2} + \underset{\text{Potassic hydrate.}}{2OKH} = \underset{\text{Potassic sulphate.}}{S^{VI}O_2Ko_2} + \underset{\text{Water.}}{2OH_2}.$$

Acids are also as a rule remarkable for their acid taste, and for the power they possess of reddening vegetable colours, such as litmus (the ordinary test for an acid).

When an acid contains oxygen its name is generally formed by adding the terminal *ic*, either to the name of the element with which the oxygen is united, or to an abbreviation of that name, *e.g.*, carbonic acid, $\mathbf{C}OHo_2$; nitric acid, $\mathbf{N}^{v}O_2Ho$. But when the same element forms two acids with oxygen, the name of that containing less oxygen is distinguished by the termination *ous*, *e.g.*,

Sulphurous acid, $\mathbf{S}^{iv}OHo_2$; sulphuric acid, $\mathbf{S}^{vi}O_2Ho_2$.

If the same element forms more than two acids with oxygen, the prefixes *hypo* and *hyper* or *per* are used, as in the cases of hyposulphurous ($\mathbf{S}^{vi}S''OHo_2$), and perchloric acids $\left(\left\{\begin{matrix}\mathbf{O}Cl\\O\\\mathbf{O}Ho\end{matrix}\right.\right)$.

In some acids the place of oxygen is taken by sulphur; this peculiarity is expressed by the prefix *sulpho* or *sulph*, the terminals *ous* and *ic* being used, just as in the case of oxygen acids, *e.g.*,

Sulpharsenious acid, $\mathbf{As}'''(S''H)'_3$;
Sulpharsenic acid, $\mathbf{As}^{v}S''(S''H)'_3$.

Other acids consist of hydrogen and some other element; since no element is known to form more than one acid with hydrogen, the names of these end in *ic*, whilst they have the prefix *hydro* or *hydr*, *e.g.*,

Hydrochloric acid, HCl.
Hydriodic acid, HI.

To the residue obtained by the abstraction of water from one or two molecules of an oxygen acid, the term *anhydride* or *anhydrous acid* (v. p. 72) is given, *e.g.*,

$\mathbf{S}^{iv}OHo_2$	$-$	$\mathbf{O}H_2$	$=$	$\mathbf{S}^{iv}O_2$.
Sulphurous acid.		Water.		Sulphurous anhydride.
$\mathbf{S}^{vi}O_2Ho_2$	$-$	$\mathbf{O}H_2$	$=$	$\mathbf{S}^{vi}O_3$.
Sulphuric acid.		Water.		Sulphuric anhydride.

The term *base* is applied in mineral chemistry to three classes of compounds, all of which are converted into salts by the action of acids.* These are—

1st. Certain compounds of metals with oxygen, such as sodic oxide ($\mathbf{O}Na_2$), zincic oxide ($\mathbf{Zn}''O$), &c.

2nd. Certain compounds of metals with the compound radical hydroxyl ($\mathbf{O}H$ or Ho), such as sodic hydrate ($\mathbf{O}HNa$ or NaHo), zincic hydrate ($\mathbf{Zn}''Ho_2$), &c.

3rd. Certain compounds of nitrogen, phosphorus, arsenic, and antimony, such as ammonia ($\mathbf{N}'''H_3$).

The bases of the first class are named in accordance with the rules for binary compounds; some, however, still retain their irregular names; the chief of these are baryta, strontia, lime, magnesia, and alumina.

To the bases of the second class the name of *hydrates* is given. The irregular names—potash and soda—are, however, often used instead of the systematic names, potassic and sodic hydrate.

The bases of the third class (except ammonia), are distinguished by the terminal syllable *ine* (*e.g.*, methylamine).

A *salt* is produced, as has been already stated, when an acid† and a base act upon each other. Salts which are binary compounds free from oxygen and sulphur, like common salt (NaCl), are called *haloid salts;* a salt containing oxygen may be characterised as an *oxy-salt;* whilst, if this oxygen be replaced by sulphur, it is a *sulpho-salt.*

The haloid salts are named according to the rules for binary compounds.

The nomenclature of oxy-salts will be sufficiently illustrated by the following examples:

* A few acids do not convert bases into salts; *e.g.*, hydrosulphuric acid, which produces sulphides.

† A few acids must be excepted, especially hydrosulphuric acid, as sulphides must be regarded as having more in common with oxides than with salts.

Potassic phosphate..... $\mathbf{P}^{v}OKo_3$.
Hydric sodic sulphate ..... $\mathbf{S}^{vi}O_2HoNao$.
Dihydric sodic phosphate ..... $\mathbf{P}^{v}OHo_2Nao$.
Hydric ammonic sodic phosphate.. $\mathbf{P}^{v}OHo(NH_4O)Nao$.

Binary Compounds. Supplementary Rule. The directions given above (p. 71), for assigning names to binary compounds which possess both a basylous and a chlorous constituent, may be modified so as to apply also to the less common cases in which both parts of the compound are basylous, or both chlorous: such are—

Silicic hydride ..... $\mathbf{Si}^{iv}H_4$.
Selenious chloride ..... $\mathbf{Se}^{iv}Cl_4$.
Chloric peroxide ..... $\left\{\begin{matrix}\mathbf{O}Cl\\O\\O\\\mathbf{O}Cl\end{matrix}\right.$.

Chapter VIII.

OXYGEN, O_2.

Atomic Weight and Sp. Gr. = 16. *Molecular Weight* = 32. *Molecular Volume* □□. 1 *litre weighs* 16 *criths. Equivalence* ii.

Occurrence. Oxygen* was discovered in 1774 by Priestley, and a year later independently by Scheele. It is the most abundant and important element in our globe; but, on account of its exceedingly strong negative or chlorous energy, by far the largest part of the earth's oxygen exists in the combined state in the solid portion of our planet. But oxygen is also the most important constituent of the atmosphere: about 23 parts per cent. by weight, or 20·9 per cent. by volume, of pure and dry atmospheric air consist of oxygen. This element forms also $\frac{8}{9}$ths by weight of water, and is an essential constituent both of animal and vegetable organisms.

Preparation. 1. From the atmosphere oxygen may be obtained pure by the following interesting process, which is, however, far too expensive to be of any practical value; heat a small quantity of mercury, at a temperature just below its boiling point (350° C.), for three or four days, in a flask to which atmospheric air has access. Oxygen is absorbed and the metal is converted into red scales of mercuric oxide. These on being raised to a temperature of from 370° C. to 400° C. yield up their oxygen again in a state of purity.

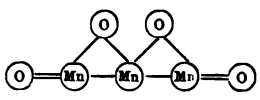
* ὀξύς, acid; γεννάω, I produce. So-called because oxygen produces with many other elements acids.

This was the original method pursued by Priestley, and is explained by the accompanying formula:

$$2Hg + O_2 = 2\underset{\text{Mercuric oxide.}}{Hg''O} = 2Hg + O_2.$$

2. The mineral pyrolusite, also known as "black oxide of manganese," or manganic oxide, heated to redness in an iron bottle or retort, yields a good supply of oxygen:

$$\underset{\text{Manganic oxide.}}{3Mn^{iv}O_2} = \underset{\text{Trimanganic tetroxide.}}{\begin{cases} {}'Mn'''O \\ {}''Mn''\ O \\ {}'Mn'''O \end{cases}} + O_2.$$



3. Potassic chlorate heated in a Florence flask, or a retort of hard glass, fuses and then evolves all its oxygen in a state of great purity. If about one-fourth of its weight of manganic oxide be mixed with this salt, the gas is emitted at a lower temperature but in a state of less perfect purity, some chlorine being also liberated. The manganic oxide is found unchanged at the end of the operation.

$$\underset{\text{Potassic chlorate.}}{2\begin{cases} OCl \\ O \\ OK \end{cases}} (+ Mn^{iv}O_2) = \underset{\text{Potassic chloride.}}{2KCl} + 3O_2 (+ \underset{\text{Manganic oxide.}}{Mn^{iv}O_2}).$$

4. Concentrated sulphuric acid heated with half its weight of powdered manganic oxide, liberates half the oxygen of the latter:

$$\underset{\text{Sulphuric acid.}}{2S^{vi}O_2Ho_2} + \underset{\text{Manganic oxide.}}{2Mn^{iv}O_2} = \underset{\text{Manganous sulphate.}}{2S^{vi}O_2Mno''} + \underset{\text{Water.}}{2OH_2} + O_2.$$

5. The following reaction, which takes place when potassic bichromate and sulphuric acid are mixed and heated in a glass retort, also affords a supply of oxygen:

$$2\left\{\begin{matrix}{}'\mathbf{Cr}^{v}O_2Ko\\ O\\ {}'\mathbf{Cr}^{v}O_2Ko\end{matrix}\right. + 8\mathbf{S}^{vi}O_2Ho_2 = 2\mathbf{S}^{vi}O_2Ko_2 +$$

Potassic bichromate. Sulphuric acid. Potassic sulphate.

$$2\left(\begin{matrix}\mathbf{S}^{vi}O_2\\ \mathbf{S}^{vi}O_2—('Cr'''_2O_6)^{vi}\\ \mathbf{S}^{vi}O_2\end{matrix}\right) + 8\mathbf{O}H_2 + 3O_2.$$

Chromic sulphate. Water.

6. In the electrolysis of water (see p. 41) oxygen is liberated at the positive pole.

7. Steam and chlorine when passed through a red-hot porcelain tube are transformed into hydrochloric acid and oxygen :—

$$2\mathbf{O}H_2 + 2Cl_2 = 4HCl + O_2.$$

8. Many oxides, nitrates, &c., evolve oxygen when heated.

Numerous other methods of preparing this gas have been proposed, but none of them are as yet of much practical moment.

Properties. Oxygen is a transparent, colourless, inodorous, and tasteless gas; its specific gravity is 16 (air standard 1·105), so that it is slightly heavier than atmospheric air. Its refracting effect on light is less than that of any other known substance. All attempts to liquefy it have failed. Water takes up a rather larger bulk of oxygen than of hydrogen: viz., at 0° 4 per cent., at 10° 3¼ per cent., and at 20° 2·8 per cent. of its volume. On the solution of this small quantity of oxygen depends the existence of fishes and most other forms of animal life in the waters of rivers, lakes, and seas. Fishes pass water continually through their gills, in which the oxygenation of their blood takes place. Oxygen has decided magnetic properties, like those of iron but much weaker; the ratio of the magnetism of oxygen to that of iron is as 1 to 2647. This property, by virtue of which a

collodion balloon filled with the gas is attracted by a large magnet, is—as in the case of iron—diminished or for the time destroyed by an elevation of temperature. Dr. Faraday has sought to show that the diurnal variations of the compass are caused by the alternate heating and cooling of the oxygen of the atmosphere.

Oxygen is the great supporter of animal life and combustion, and is therefore a necessary and the most important constituent of atmospheric air, in which it exists diluted with nitrogen, which plays no part in supporting either combustion or life, but that of making the action of the oxygen less rapid and intense. Pure oxygen and atmospheric air support combustion in very different degrees, for example: a burning splinter of wood when blown out continues to glow in the air, but rekindles with a sharp noise and burns with greatly increased rapidity and brilliancy when plunged into oxygen; the flame of phosphorus, which burns brightly when kindled in air, is insupportably brilliant in oxygen; sulphur also burns with comparative brilliancy and energy in oxygen, and charcoal with an intense glow and beautiful scintillations; a diamond will also burn in oxygen, leaving only carbonic anhydride; an oil lamp the flame of which is smoky in air gives a clear and brilliant flame in oxygen; and many metals, such as iron and steel, zinc, aluminium, potassium, &c., burn brilliantly when heated and plunged into the gas,—whilst the tranquil oxidation they undergo in the air is a comparatively slow combustion,—though, especially in moist air, it is often attended by an elevation of temperature so considerable as to be very apparent,—for example, when a heap of iron turnings moistened with water is left to rust. Pure oxygen differs from diluted oxygen in a similar manner in its effect on life: a small animal placed in a vessel full of oxygen soon dies of the excessive excitement produced by a too rapid oxidation of its blood. The change in colour which takes place in the blood of animals as it passes through their lungs is due to the absorption of oxygen, which converts purple venous into

bright red arterial blood. Since animals return this oxygen from their lungs to the atmosphere in combination with carbon as carbonic anhydride, the store of free oxygen would eventually become reduced, were it not that the leaves of plants, absorbing in their turn the carbonic anhydride produced in animal organisms, assimilate its carbon and liberate oxygen in a state of purity, thus replenishing the supply required for the support of animal life. This fact may be readily proved by exposing to the action of sunlight, for several hours, some fresh green leaves in jars filled with water in which some carbonic acid is dissolved; several cubic inches of oxygen may be collected in this manner. The chemical affinity of oxygen for other elements, whether basylous or, like itself, chlorous, is very great indeed; fluorine is the only element no compound of which with oxygen is yet known. The intense chemical attraction of oxygen for hydrogen has already been noticed. The energy with which various other substances combine with this gas will again engage our attention under the head of combustion.

The purity of oxygen may be roughly estimated by the degree of sharpness with which a glowing splinter of wood bursts into flame when plunged into the gas. Pure oxygen is completely absorbed by a solution of pyrogallic acid in strong potash. With nitric oxide, oxygen gives red fumes of nitric peroxide. When two volumes of hydrogen are mixed with one of oxygen and exploded, water only remains; and this compound alone is formed when hydrogen is burnt in oxygen, or oxygen in hydrogen:

$$2H_2 + O_2 = 2OH_2.$$

OZONE, O_3.

Molecular Weight = 48. *Molecular Vol.* $\square\square$.

This name has been rashly or ignorantly applied to several very different substances, though it belongs properly to a

remarkable gas—an allotropic* form of oxygen—which Professor Schönbein named ozone (ὄζω, I smell) on account of its peculiar odour, an odour which is perceived when electric sparks are passed through dry oxygen or air.

Preparation. Ozone has never been isolated and examined in a state of purity; but Mr. Siemens has invented an apparatus for converting oxygen into ozone by electric induction, by means of which it is said that from 10 to 15 per cent. of a quantity of ordinary oxygen may be transformed into its modified form. Some ozone is likewise produced in the electrolytic decomposition of water, and also when a stick of phosphorus is left for a short time in moist air.

Properties. Ozone is a transparent colourless gas; it has the strong odour above mentioned, besides possessing an irritating action on the lungs; its specific gravity is 24, according to M. Soret, whose recent investigations appear conclusively to prove that the density of ozone is to that of oxygen as 3 to 2. Ozone is insoluble in water.

Ozone is reconverted into oxygen at 100°; at about 290° the change is instantaneous. It is a most powerful oxidising agent, has strong bleaching and disinfecting powers, corrodes cork, caoutchouc, and other organic substances, and rapidly oxidises iron, copper, and even silver, when moist, as well as dry mercury and iodine. In all these cases, and in the absorption of the gas by potassic iodide, no contraction of volume appears to take place; that is, the residual gas occupies just the same volume during and after such absorbing actions as the mixture of oxygen and ozone occupied at the outset. This fact is explained by the following considerations. Oxygen when ozonised diminishes in volume; the density of the ozone formed is to that of the oxygen as 3 to 2; thus the volume occupied by three atoms of ozone is the same as that occupied by two atoms of oxygen,—and, if Ampère's Law of Vapour Volumes holds true here, the mole-

* ἄλλος, another; τρόπος, fashion or guise.

cule of ozone must consist of three atoms of oxygen, since that of ordinary oxygen consists of two atoms, and the following graphic formula must represent correctly the molecule ozone:

Further, when ozone exerts its oxidising functions, in such cases as those cited above, the action which takes place is no doubt the following:—from every molecule of ozone only one atom is liberated, the remaining two atoms forming a molecule of ordinary oxygen and expanding to the normal molecular volume, so as to occupy exactly the same space as that before taken up by the molecule O_3: *e.g.*,

$$\underset{\text{Ozone.}}{O_3} + \underset{\text{Potassic iodide.}}{2KI} + \underset{\text{Water.}}{OH_2} = \underset{\text{Potash.}}{2OKH} + \underset{\text{Oxygen.}}{O_2} + \underset{\text{Iodine.}}{I_2}.$$

These facts are established by M. Soret's experiments with essence of turpentine and essence of cinnamon; both of these liquids possess the remarkable property of entirely absorbing ozone, without either decomposing it or absorbing the ordinary oxygen with which ozone is always mixed.

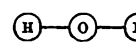
Some persons have assumed that to the action which ozone effects upon papers moistened with potassic iodide and starch, in liberating the iodine, and thus imparting a blue colour to the starch, the fact that on exposure in the atmosphere such papers sometimes turn blue is to be ascribed. Unfortunately for this hypothesis, many gases and acids which are known to be common impurities in our atmosphere produce the same effect; the test is, therefore, perfectly unreliable; and, till a better test is discovered, we cannot know whether ozone is ever present in the air in perceptible quantities, or whether there is truth in the supposition that its presence is of importance to the salubrity of the atmosphere.

Chapter IX.

COMPOUNDS OF HYDROGEN WITH OXYGEN.

These are two in number: Water, which possesses by far the greater practical importance, and hydric peroxide.

WATER—HYDRIC OXIDE.



OH_2.

Molecular Weight = 18. *Molecular Volume* □□. 1 *litre of water-vapour weighs* 9 *criths. Fuses at* 0°. *Boils at* 100°.

The qualitative composition of this exceedingly abundant compound was unknown and water was regarded as an element till the year 1781, when Cavendish observed that it is produced on burning hydrogen in air, or when a volume of oxygen is exploded with two of hydrogen (v. pp. 43, 44).

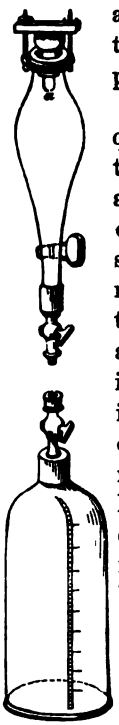
The quantitative composition of water may be determined exactly by either of two methods, *synthesis* or *analysis*,* by building up its molecules or by taking them to pieces.

Synthesis of Water. 1. The following is the process invented by Cavendish for obtaining a considerable quantity of water by the direct union of the gases oxygen and hydrogen: A stout glass vessel (an improved form of which is shown in fig. 4) is exhausted and then filled with a mixture of the gases in the proportion of two volumes of hydrogen to one of oxygen; the stop-cock is then closed; and, by means of two

* Synthesis (*σύνθεσις*, a putting together): analysis (*ἀνάλυσις*, a loosing).

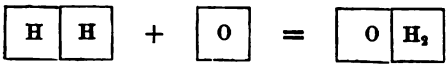
platinum wires melted through the glass (*a* fig. 4), the electric spark is passed, producing a flash of light, after which the sides of the vessel are found to have become covered with moisture; into the vacuous space left by the explosion a fresh supply of the mixed gases is admitted and exploded by the spark, and the repetition of this process several times affords a quantity of perfectly pure water.

Fig. 4.



To use the direct combination of water as a quantitative method of determining the composition by volume of water it is necessary to employ a long, accurately graduated tube of strong glass, called a *eudiometer* (*εὐδία*, calm air; *μέτρον*, a measure), closed at one end, through which two platinum wires have been melted. After filling this tube with mercury and plunging the open end into a mercurial trough, hydrogen gas is admitted into it, and the volume of the gas is read off. Oxygen is next admitted in smaller quantity, the volume of the mixed gases is noted, and then, whilst the mouth of the tube—which should not be more than half full of gas—is pressed down on a plate of caoutchouc placed under the mercury, the spark is passed. When the tube has cooled, and its sides have become bedewed with water, its mouth is raised from the caoutchouc, and the mercury is allowed to rise and take the place of the exploded gases; finally the volume of the residual gas is observed. If the volume of hydrogen admitted was 100 volumes, and that of oxygen 75 volumes, the gas which remains will be found to be pure oxygen, and to occupy 25 volumes. Thus it is shown that two volumes of hydrogen combine with exactly one volume of oxygen to form water. It may further be proved, by conducting the experiment at a temperature above 100° C. that the volume of the gaseous water or steam formed in such an ex-

periment is exactly 100 volumes; so that two volumes of hydrogen combine with one of oxygen to form two of aqueous vapour:—



2. Another mode of obtaining water by synthesis is the reduction of some metallic oxide, such as cupric oxide, to the metallic state by heating it to redness in a current of dry hydrogen:—

$$2\mathbf{Cu}''O + 2H_2 = Cu_2 + 2\mathbf{O}H_2.$$

To determine the proportions by weight in which the oxygen and hydrogen combine: weigh the cupric oxide before the operation; condense and otherwise arrest all the water produced and weigh it; and ascertain what loss the cupric oxide has sustained at the end of the experiment. Let this loss be 8 grammes, the weight of water produced will be 9 grammes; so that it is evident that 1 gramme of hydrogen combines with exactly 8 grammes of oxygen.

Analysis of Water. The processes for the production of hydrogen that we have described (pp. 40, 41), except the first and third, are all modes of analysing water.

Distilled Water. Distillation is always resorted to for obtaining pure water for chemical purposes. A copper still, with a copper or block tin worm, is usually employed; no leaden piping must be used, since lead is freely soluble in pure water containing only oxygen in solution.

Properties of Pure Water. It is a clear, transparent, inodorous, and tasteless liquid. When seen in small quantities, or when light is transmitted through but a small thickness or depth of water, it appears to be quite colourless; but when light passes through a thicker stratum some of the rays are arrested, and the light which issues has a bluish-green colour—the colour of the lakes of Switzerland and Norway

and of glaciers (as seen in crevasses and ice-caves). Dr. Frankland has shown that, owing to the presence of quantities of brown peaty or yellow sooty matter, this beautiful natural hue cannot be fully seen in the water of this country until after distillation, but that distilled water always presents this characteristic bluish-green tint. The specific gravity of pure water at 15°·5 (in France at 4°) is taken as unity, and is the standard to which the specific gravities of liquids and solids are referred. The weight of a cubic metre of distilled water at 4° is 1,000 kilogrammes; that of a litre is 1,000 grms.; and that of a cubic centimetre at the same temperature is 1 grm. Since a cubic metre of air, at 0° and 760 mm. pressure, weighs 1·2932 kilogrms., water is about 773 times heavier than air. Like other liquids, water is almost incompressible; a million volumes of water contract under the pressure of one atmosphere only by 51½ volumes. The latent heat of water is 79·25 (Person); its absorbing action on radiant heat is greater than that of any other known liquid. The specific heat of water is unity, since water is adopted as the standard; it is greater than that of any known substance, except hydrogen,—a property of the highest importance in contributing to the absence of extremes of temperature, especially in islands. In summer the water of our oceans, in rising through a few degrees of temperature, absorbs a vast quantity of heat, and keeps the atmosphere above and around it cool,—whilst in winter, by slowly parting with this store of force, it secures a mild temperature in remarkable contrast with the intense cold which characterises the centre of a continent in winter. The same causes operate to a minor extent in the alternations of day and night. The specific heats of water and air being 1 and 0·237 respectively, a pound of water in cooling through one degree warms 4·16 lbs. of air one degree; and a litre of water in losing one degree raises about 3216 litres of air one degree, since the weight of a litre of water is about 773 times that of a litre of air. The high specific heat of water may be illustrated by the following ex-

periment:—To a pound of water at 100° add six pounds of mercury at or below 15°; after thoroughly stirring the water with the mercury only a very slight diminution of temperature can be perceived. We have already had occasion to notice one anomaly in the effect of heat upon water, namely, that when water at 0° is heated it contracts till it reaches a temperature of 4°, which is the point at which it occupies the smallest volume, and then begins to expand,—and *vice versâ*. It is also anomalous that ice contracts on melting, whilst water at 0° expands to form ice, so that crystals of ice float on the water in which they form. In fact the specific gravity of ice is only 0·918.* These properties of ice and water are very important: during periods of cold, rivers and lakes are soon reduced, by the continued sinking of the colder and therefore heavier water at the surface, and its incessant replacement by warmer water from below, to a uniform temperature of 4°; but, after passing this turning-point, the surface water expands and becomes lighter the more it is cooled, and no longer sinks, and, whilst the lower strata of water remain at 4°, it freezes; and the ice, having a lower specific gravity than the water from which it is formed, stays at the surface protecting the water and its inhabitants, animal and vegetable, from further reduction of temperature. These facts may be illustrated by a simple experiment:—Place in a tall jar, full of water, two thermometers, one at the surface and the other at the bottom, and cool the jar from the ordinary temperature to the freezing-point; the surface thermometer will indicate a higher temperature than the lower one, till the latter marks 4°; the upper thermometer will then continue to fall, not only till it reaches 4°, but down to zero, whilst the other continues to mark 4°. Though 0° is its freezing-point, water may be cooled without solidifying to — 12°, if care is taken to preserve it from agitation; but the slightest shake determines the congelation of the mass, and this is accompanied by a rise of

* 0·94 (Naquet).

temperature to 0° due to the evolution of latent heat. The latent heat of liquefaction of ice is 79·25; that is, to liquefy ice you want as much heat as would raise the same weight of water 79°·25, or as would raise 79·25 times its weight of water one degree in temperature. Owing to its great depth the ocean does not require the same provision to impede its solidification; and sea-water, having a greater density than fresh water, continues to contract even beyond the point at which it freezes (– 2°·55), expanding suddenly, however, on solidification. The great expansion of ice at the moment of solidification is the cause of the bursting of water-pipes in a frost. A small quantity of water inclosed in a strong iron bottle suffices, when cooled to the freezing-point, for the bursting of the bottle. The freezing of water in crevices is an important cause of the disintegration of rocks. The crystalline forms of ice are numerous, and are derived from the rhombohedron and six-sided prism. When two pieces of melting ice are placed in contact they freeze together, exhibiting the phenomenon of *regelation;* pressure assists though it seems not to be necessary to regelation; and under pressure a quantity of small pieces freeze together to form a mass of transparent ice of any shape which a mould can communicate to it. Many of the phenomena of glaciers are due to this remarkable property of ice. Snow is probably formed by the direct solidification of the vapour of water. Snow, ice, and water evaporate at all known temperatures, forming vapour of water, which is transparent and colourless, and has a specific gravity of about 9 (air std. 0·622), since its molecule occupies the normal vapour volume; its absorbing action on radiant heat is greater than that of any other vapour; the aqueous vapour in the earth's atmosphere has generally an absorbing action on rays of heat 70 times that of the air in which it is diffused;* its

* These statements are based on some apparently conclusive experiments of Prof. Tyndall; Prof. Magnus has, however, pointed out in a recent paper what he conceives to be a source of error in these experiments, and believes that his own researches on the subject lead to the

latent heat is about 540 (536·9, Andrews): hence the great store of force or *possible motion* in water and its wide application in converting into mechanical power the heat of a coal-fire; at 0° its tension or elastic force, expressed in millimetres of a column of mercury it could support, is 4·6 mm., at 30° 31·548 mm., at 60° 148·791 mm., at 85° 433·041 mm., and at 100° 760 mm. (v. pp. 33, 34). Hence the boiling-point of water is 100°, as this is the point at which the tension of its vapour is equal to the normal atmospheric pressure; but under reduced pressure water boils at a lower temperature; for instance, if a flask of water be boiled over a lamp and then removed, corked up, and plunged into cold water, the water will recommence boiling,—the reason being that, when the aqueous vapour which filled the upper part of the flask is made to condense, the pressure within the flask becomes less than the ordinary atmospheric pressure, and less than the tension of the vapour of the hot water. Similarly, water has been found by Prof. Tyndall to boil at the top of Mont Blanc and Monte Rosa at about 85°. The lowering of the boiling-point is determined by Prof. Tyndall to be about 1° for every 1062 feet (323·68 metres) that we ascend. The solvent power of water on solids, liquids, and gases will be repeatedly illustrated as we proceed. But a few facts with respect to the solubility of solids—especially of salts—must be given here. Most salts dissolve in water to a greater or less extent, and, when the water is evaporated, separate again in the crystalline form. This crystallisation of salts from their solutions is constantly employed for their purification. The application of heat generally promotes the solubility of solids in water, but not always; for instance, common salt is equally soluble at all temperatures; and sodic sulphate, though its solubility rises rapidly from about 4 parts in 100 of water at 0° to 53 parts in 100 at 34°, above 34° becomes slightly less soluble.

Water is a perfectly neutral substance. It enters into

conclusion that "aqueous vapour has no very great power of thermic absorption."

chemical combination in a characteristic and peculiar manner both with anhydrides and with bases, to form acids and hydrates, *e.g.*,

$$\underset{\text{Sulphuric anhydride.}}{S^{vi}O_3} + OH_2 = \underset{\text{Sulphuric acid.}}{S^{vi}O_2Ho_2}. \quad \underset{\text{Potassic oxide.}}{OK_2} + OH_2 = \underset{\text{Potash.}}{2OKH}.$$

But water also associates itself with many substances, especially salts separating from their solutions, in another totally different manner; when existing with compounds in this form of union it is called *water of crystallisation: e.g.*, ferrous sulphate, $S^{vi}OHo_2Feo''$, $6OH_2$. Water of crystallisation cannot be considered as ever existing in ordinary chemical combination with substances; though they are united to this water in fixed and definite proportions, the force which causes its association with them is perhaps not the chemical force, but possibly a peculiar form of cohesion. By the application of a gentle heat water of crystallisation may be driven off from salts without impairing their chemical properties, though the loss of this water causes their crystals to crumble to powder. Salts which part with their water of crystallisation on mere exposure to air are called *efflorescent*. Such are sodic sulphate — $S^{vi}O_2Nao_2,10OH_2$; and sodic carbonate — $CONao_2,OH_2$. *Deliquescent* salts are such as have so great an attraction for water, that they absorb it from the atmosphere till they become moist or even liquid, being dissolved in the water they have arrested, *e.g.*, potassic carbonate, $COKo_2,2OH_2$; calcic chloride, $Ca''Cl_2$; and magnesic chloride, $Mg''Cl_2$.

Natural Waters.—Since so large a proportion of substances are soluble in water, it is never met with in nature in a state of purity. Hence there are various kinds of Natural Waters, and we must next consider successively the properties and peculiarities of each kind.

Rain water is the purest form in which water is found; but it always contains air, and whatever gaseous impurities were present in the air through which it fell.

Spring water always contains salts, varying with the composition of the rocks, the strata, or the soil through which it has percolated. The commonest saline impurities are the calcic and magnesic carbonates and sulphates, and sodic chloride (or common salt).

Calcareous waters are those in which much calcic carbonate is held in solution. Since marble, limestone, oölite, and chalk consist of little else besides calcic carbonate, calcareous springs abound wherever these formations exist. Each gallon of pure water does not dissolve much more than about two grains (and each litre 0·028 grm.) of calcic carbonate; but water containing much carbonic acid in solution will take up this salt in far larger quantities.* It is by the escape of carbonic anhydride from calcareous waters, that stalactites, stalagmites, tufa, travertine, and other masses of crystallised calcic carbonate are formed. The inconveniences attendant on the presence of much of this salt in water, and the modes of obviating them, will be described presently.

Mineral water is the name applied to spring waters containing in solution so considerable a quantity of inorganic matters that they impart a peculiar taste, or more or less decided medicinal qualities. According to the substances they contain they are distinguished, as: *chalybeate*, (Χάλυψ, steel,) containing salts of iron, which give an inky taste; such are the waters of some of the Cheltenham springs; *effervescent* when, owing to saturation at considerable depths and under great pressure with carbonic anhydride, they

* "Most spring waters are charged with a notable proportion of carbonic acid which dissolves a considerable amount of carbonate of calcium; the calcareous springs in the neighbourhood of London contain from 18 to 20 grains of chalk per gallon, 6 or 8 grains of which become separated by exposure of the water to the atmosphere, so that a running stream will seldom contain more than 12 or 14 grains of chalk per gallon in solution. Waters which have filtered through chalk also often contain carbonate of sodium in considerable quantity, as is the case with the deep well waters of London."—(Dr. Miller's Chemistry, vol. ii, p. 39).

evolve this gas freely,—Seltzer water for example; *sulphurous* or *hepatic* (ἡπατικός, diseased in the liver), when sulphuretted hydrogen is present in solution, communicating to the water a nauseous taste and the smell of rotten eggs, as is the case with the Harrogate water; *saline* when purgative salts are abundantly held in solution, such as magnesic sulphate, which abounds in the Epsom springs.—Many mineral springs have a temperature considerably above that at the surface of the earth. Some have a temperature of between 70° and 90° (158° and 194° F.), rising either near volcanoes or from great depths.

River water, even when not polluted as it too frequently is by sewage, is less fitted than spring water for domestic uses, owing to the drainage from manured land and the organic matter of vegetable origin which it contains in solution, and to the numerous impurities present in suspension. In the absence of town-drainage it is, however, generally wholesome, thanks to the remarkable tendency of running water to purify itself. Some notable cases of river and lake water enjoying an almost perfect freedom from impurities, have been observed; for example, only $\frac{1}{20}$th of a grain of solid matter per gallon is found in water from the river Loka, in Sweden, running over granite; and the water of Loch Katrine does not contain more than $2\frac{1}{2}$ grains of solid matter per gallon.

Sea Water. The following approximate statement of the results of Schweitzer's analysis of the water of the British Channel, and Usiglio's analysis of that of the Mediterranean (which, owing to the great extent of surface for evaporation as compared to the depth, is more salt than the open ocean), will give the best idea of the composition of sea water. Sea water contains from 3·5 to 4 per cent. (or from 2,400 to 2,800 grains per gallon) of salts, and has a mean specific gravity of 1·027. The Dead Sea contains 16,000 grains and the River Jordan 73 grains of solid matter per gallon. In Russia there is a lake—of which use is made for the extraction of salt—the depth of which is only 15 inches, and which in summer is covered with a crust of white saline matter.

COMPOSITION OF SEA WATER.

	British Channel.	Mediterranean.
Water.....	963·74	962·35
Sodic chloride	28·06	29·42
Magnesic chloride.	3·67	3·22
Magnesic sulphate	2·29	2·48
Calcic sulphate ..	1·41	1·36
Potassic chloride..	0·77	0·50
Magnesic bromide.	0·03	0·56
Calcic carbonate..	0·03	0·11
Iodine	traces	—
Ammonia.....	traces	—
Ferric oxide.....	—	a trace
	1000·00	1000·00

The ice formed on freezing sea water incloses but a very small proportion of these salts, so that, on melting, it produces tolerably *sweet* as distinguished from *salt* water. Perfectly pure water may be obtained by subjecting sea water to distillation.

It is from the small percentage of magnesic bromide contained in the ocean that bromine is extracted; whilst marine vegetation is the source from which we draw our supply of iodine (v. chap. xiv).

Chapter X.

WATER (*continued*).

Purification from Natural Impurities and Artificial Contaminations. This important subject is the next which presents itself for consideration with reference to water.

Natural Impurities. *i. Suspended Impurities*, consisting of inorganic substances, organic remains, and living organisms, are present in most waters, especially in river water. By mechanical filtration, through sand for example, they may be removed, with the exception of the ova of living organisms; these pass through such a filter and are subsequently hatched. The more deleterious suspended impurities are removed with greater certainty if animal charcoal be used in addition to the sand.

ii. Mineral Impurities in Solution. Those which are of common occurrence are already enumerated under the head of spring water. The most important are the calcic and magnesic carbonates, which give to water the property usually called *hardness*, causing it to curdle soap in the process of washing, by producing with the fatty acid of the soap a precipitate of calcic stearate, and fixing this greasy substance in the pores of the skin just in the same manner that the dyer precipitates and fixes his colours in calico. Pure water, or water free from these salts, dissolves soap, producing on agitation a *lather*, and is called *soft*. The comparative hardness of different waters may be ascertained with admirable ease and fair precision by means of *Dr. Clark's soap-test*, the principle of which is this: a standard solution of soap in proof-spirit is made (containing about 120 grs. of curd-soap to the gallon). One grain of chalk in one imperial gallon

(one part in 70,000 parts) of water, or a corresponding amount of any other salt of calcium, constitutes one degree of hardness on Dr. Clark's scale. To test the hardness of a given water introduce 1,000 measured grains of it into a bottle which will hold five ounces, accurately fitted with a glass stopper. Add the soap solution to the water from a graduated tube, called a *burette*, each division of which should correspond to 10 water-grains. One form of burette is represented in fig. 5. After each addition of the soap-test, replace the stopper in the bottle, shake the bottle briskly for a minute, and then lay it upon its side; add fresh portions of the soap solution until a fine lather in uniform small bubbles remains unbroken over the surface for three minutes; this indicates that the calcic salt has been precipitated as stearate, and that there is a slight excess of soap in the solution. By the number of measures of soap-test which have been added, the degree of hardness is determined according to the annexed table. If the water exceeds 16° in hardness it should first be diluted with its own measure or even twice or thrice its bulk of distilled water. An account in greater detail of this useful method of testing water will be found in a foot note in Dr. Miller's Chemistry (vol. ii, p. 491), whence this sketch has been extracted.

FIG. 5.

A more convenient "*degree of hardness*,"—viz., one part of chalk or its equivalent of other hardening material in 100,000 parts of water—is also frequently used. For every degree of hardness on this scale, 100,000 parts by weight of the water would destroy 12 parts of the best hard soap. Such degrees are converted into degrees on Dr. Clark's scale by multiplying by 7, and then moving the decimal point one place to the left.

Dr. Clark's Table of Hardness of Water.

Degree of hardness.	Measures of soap-test.	Difference for next 1° of hardness.
0 (Distilled water)	1·4	..... 1·8
1	3·2	..... 2·2
2	5·4	..... 2·2
3	7·6	..... 2·0
4	9·6	..... 2·0
5	11·6	..... 2·0
6	13·6	..... 2·0
7	15·6	..... 1·9
8	17·5	..... 1·9
9	19·4	..... 1·9
10	21·3	..... 1·8
11	23·1	..... 1·8
12	24·9	..... 1·8
13	26·7	..... 1·8
14	28·5	..... 1·8
15	30·3	..... 1·7
16	32·0	

Thus we see that, whilst a few drops of soap-test produce a permanent lather in 1,000 grains of distilled water, 32 measures or 320 water-grains are necessary in order to effect this object in the same quantity of water containing 16 grains of calcic carbonate per gallon.

Five methods, by means of which the hardness of water may be mitigated or removed, have been proposed:—

(*a.*) *Distillation* effects this object perfectly, but its expense renders the method out of the question where absolute purity is not essential. *Congelation*, repeated several times, may be resorted to in the Arctic regions to free sea-water almost completely from the salts it contains.

(*b.*) *Boiling* has the effect of expelling the carbonic anhydride to which the solution of the calcic carbonate is due, and

the salt is thrown down as a fine insoluble powder. This process is of course inapplicable on a large scale.

(*c.*) The addition of *Soda-ash* (or crude sodic carbonate) which combines with the carbonic acid forming sodic bicarbonate, a salt which has no hardening effect on water, precipitates the calcic carbonate.

(*d.*) In steam-boilers, where hard waters form deposits, and where consequently it is important to use only water that is soft, an alternative to the last method is the addition of *ammonic chloride* (or *sal ammoniac*), which becomes converted into ammonic carbonate, and then volatilises, while the soluble calcic chloride remains.

(*e.*) *Dr. Clark's process.* This consists in the addition of lime, which combines with the carbonic acid in the water; the carbonate formed, together with that previously held in solution by the carbonic acid, is precipitated.

In all these processes, except that of distillation, it is evident that the only salt removed, or rather the only one at all completely thrown down, is calcic carbonate; some magnesic carbonate goes down with it, but the calcic and magnesic sulphates remain and cannot be got rid of by such simple means; these sulphates are therefore said to give to water *permanent hardness* (which remains after the water has been boiled for half-an-hour), as distinguished from the *temporary hardness* due to carbonic acid and calcic carbonate.

iii. *Organic Impurities.* Those which find their way naturally into water may be almost disregarded, especially those of vegetable origin, such as the colour given by peat. These, indeed, are generally effectually removed by the exposure of the water for a few days to the action of oxygen in a reservoir. So far as their functions are at present known, the living animalcules existing in most waters are rather beneficial than otherwise.

Artificial Contaminations.—i. *Contaminations from Pipes and Conduits.* The most important of these is lead. Where new leaden pipes are used, before they become coated with a

protecting layer of carbonate, if oxygen be present in the water and carbonic acid be not abundant (less than two volumes of carbonic anhydride dissolved in every 100 volumes, a condition not, however, of very frequent occurrence), much lead is likely to become dissolved in the water, and the effects on persons drinking it may be serious, especially as lead, when taken sufficiently frequently, in however small quantities, accumulates in the system, and acts as a slow poison. The presence of oxygen in water is necessary, and the presence of ammonia is favourable to the corrosion and solution of lead; calcic carbonate in solution in carbonic acid, and phosphates exert a remarkable preservative influence in preventing the solution of lead, a film of an insoluble compound of lead being formed which protects the metal from corrosion. Two volumes of carbonic anhydride, dissolved in 100 volumes of water, completely shield even distilled water from this contamination.

ii. *Contaminations in Cisterns from Sewer Gases.* In many towns, and notably in London, the water in our cisterns, as well as the air in our houses, is polluted by the gases which we allow to enter through waste-pipes descending into drains and sewers. The arrangement to which this abominable nuisance is due is briefly this: cisterns are filled daily by means of a tap to which is fitted a ball-cock to arrest the supply of water so soon as the cistern is nearly full; just above the level where the rise of water in the cistern is thus arrested is the opening of a pipe which leads straight into a drain communicating with the sewer; lest the atmosphere of the house should, through this pipe, be placed in direct continuity with that of the drain and sewer, it is usual to make the pipe that enters the drain curved at its lower end, in the shape of the letter J; it is imagined that this bent extremity of the tube will always be kept filled by water flowing down from the waste-pipe, and will act as a tolerably effectual valve, so as to exclude the sewer-gases. But what is really the fact? On account of the very ingenious regulation of the ball-cock,

no water can ever pass into the waste-pipe at all, nor even rise to the level of its orifice; the consequence is that, if there ever was any water in the bend of the waste-pipe, it cannot have remained there long, nor can it ever be renewed; hence no valve is interposed between the atmosphere of the house and that of the drain, and fires and chimneys—creating the draft which enters the house at every chink and opening—suck into it the foul gases of the drains and sewers to pollute the air we breathe, and not only so, but also—seeing that it is across the surface of our cisterns that all these gases (many of them highly soluble in water) are dragged—to render the water which we drink, and which we associate with the idea of purity and cleanliness, unclean and deleterious.

The only cure practically applicable and fairly reliable for water thus clumsily contaminated, after it has, perhaps, for the sake of a pure supply been brought from a great distance and filtered with extraordinary care, is filtration through animal charcoal, renewed regularly at short intervals.

But, since prevention is better than cure, and (so far as I know) the only *sure* way of avoiding these dangers of contamination in towns is to allow water to be drawn straight from the mains, without the intervention of any apparatus of cisterns and waste-pipes, and to have a constant instead of an intermittent system of delivery, this plan, already followed in Manchester and some other towns, and at the public drinking fountains in London, should be universally adopted.

iii. *Contaminations from Sewage thrown into Rivers.* Animal impurities undergoing decay and oxidation are the most noxious that exist in the water supplied to towns. The chief products of the oxidation of these organic compounds are nitrates, nitrites, and ammoniacal salts, substances harmless in themselves, but in the production of which the constituent elements of organic bodies have to pass through various stages in which compounds of a hurtful character are formed. The violence of epidemic cholera in any given place has been shown by Dr. Farr to exhibit a close relation to the degree of sewage

contamination of the water supply. Dr. Frankland* believes that "the experience which we have derived from four visitations, leads irresistibly to the conclusion, that, whilst no successful barriers have been devised against the introduction of the disease into this or any other country, cholera can never establish itself as an epidemic, unless the water supply of a community be tainted with sewage impurity." By the amount of a standard solution of a pink salt, potassic permanganate, (the colour of which is destroyed by organic substances, whilst they become oxidised at its expense) required to tinge a given quantity of water with a pink hue, it may be roughly guessed whether much organic impurity is or has been present.

In order rapidly to oxidise, and thus deprive of deleterious properties, these organic contaminations, we must resort again to filtration through animal charcoal (v. p. 131) as the best, though by no means a perfect safeguard.

Uses of Water. For drinking, culinary, and washing purposes, the invaluable and indispensable necessity of pure water is universally acknowledged. For pleasantness and absence of vapidity in the taste of water, its aeration with oxygen and carbonic anhydride is necessary, as well as the absence of most organic impurities. Some injurious organic impurities have, however, no appreciable effect on the taste of water.

To plants and animals a supply of water is as essential as to ourselves. Plants assimilate the hydrogen of some of the water they imbibe—sending out from their leaves the oxygen thus liberated.

In the atmosphere the presence of aqueous vapour and its condensation in the form of clouds is believed to be of the highest importance to the maintenance of the temperateness of our climate, since the absorbing power on heat (see foot note, p. 88) of aqueous vapour, which, according to Prof. Tyndall, transcends all other gases and vapours in absorptive power—

* Lecture on the Water Supply of the Metropolis, delivered at the Royal Institution, March 29, 1867.

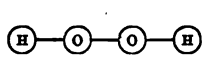
preserves us in the day from the scorching effects of the sun's direct rays, whilst at night it checks radiation from the earth into space, and prevents an excessive fall of temperature.

The protective influence exerted on the denizens of rivers, lakes, and oceans by water in the solid form of ice has already been a subject of comment.

In the form of steam, water is used as the most economical and convenient means of converting heat into mechanical motion.

The uses of water in chemistry, as a solvent, are endless.

HYDRIC PEROXIDE—HYDROXYL.

 O_2H_2 or $(HO)_2$ or Ho_2 or $\begin{cases} OH \\ OH. \end{cases}$

Molecular weight = 34.

The molecule of hydroxyl differs from that of water in the presence of a second atom of oxygen combined with the two atoms of hydrogen. Thus this compound is made up of two atoms of a monequivalent compound radical O″H or Ho. Whilst the molecule of hydroxyl, Ho_2, may therefore be called hydroxide of hydroxyl, that of water, HHo, is distinguished as hydride of hydroxyl, or hydric hydroxide—names which may be shown to be correct by the following facts:—When hydric peroxide is mixed with water which is being submitted to electrolysis, hydrogen ceases to come off, oxygen only is evolved, and water or hydride of hydroxyl is formed; further, when hydric peroxide is added to a mixture of sulphuric acid and zinc, from which hydrogen is being given off, the evolution is checked, and all the hydrogen is absorbed; the action which takes place in both cases is represented by the following formula:—

$$\underset{\text{Hydroxyl.}}{Ho_2} + H_2 = \underset{\text{Water.}}{2HHo} \text{ (or } 2OH_2).$$

An atom of this compound radical, besides existing combined with hydrogen in water, is found in a multitude of compounds, playing a very important part in their constitution and in their chemical relations to other substances. On these accounts this substance possesses great theoretical interest.

The following examples of the transference of this radical from water to other compounds will illustrate its importance:—

$\mathbf{O}K_2$	+	HHo	=	2KHo.
Potassic oxide.		Water.		Potash.
$\mathbf{Ba}''O$	+	HHo	=	$\mathbf{Ba}''Ho_2$.
Baryta.		Water.		Baric hydrate.
$\mathbf{N}^{v}{}_2O_5$	+	HHo	=	$2\mathbf{N}^{v}O_2Ho$.
Nitric anhydride.		Water.		Nitric acid.
$\mathbf{S}^{vi}O_3$	+	HHo	=	$\mathbf{S}^{vi}O_2Ho_2$.
Sulphuric anhydride.		Water.		Sulphuric acid.

In all the compounds which form the latter halves of the foregoing equations, it will be found, on reducing their molecules to a graphic representation, that to the chief atom of the compound (in the first case to the atom of potassium, in the others to the atom the symbol of which is printed in thick type,) are linked by means of one or more oxygen atoms, one or more atoms of hydrogen. The oxygen link, with its atom of hydrogen, forms an atom of hydroxyl, and is represented as such in the symbolic formula.

Now, in many of these compounds of which hydroxyl forms a part, the hydrogen of one or more of the hydroxyl atoms becomes replaced in simple chemical reactions by other elements—metals; and this apparently trivial replacement leads, even in complicated molecules, to a complete change of the properties previously enjoyed by the substance,—which, if an acid, becomes converted into a salt. Such reactions, and the compounds resulting from them, may be very simply represented by employing formulæ in which the hydroxyl of the

acid is replaced by the symbols for such compound radicals as potassoxyl, zincoxyl, &c. ($\mathbf{O}K = Ko$, $\mathbf{Zn}O_2 = Zno''$, &c.). For example:—

$$\underset{\text{Nitric acid.}}{2\mathbf{N}^{v}O_2Ho} + K_2 = \underset{\text{Potassic nitrate.}}{2\mathbf{N}^{v}O_2Ko} + H_2.$$

$$\underset{\text{Sulphuric acid.}}{\mathbf{S}^{vi}O_2Ho_2} + Zn = \underset{\text{Zincic sulphate.}}{\mathbf{S}^{vi}O_2Zno''} + H_2.$$

It is especially to be noted that the atoms of oxygen represented in the symbols of these important radicals by a small o fulfil a peculiar linking function, in virtue of which their bonds are not united to one polyad atom, but connect or link together different atoms. This power of oxygen to link together atoms is not by any means confined to compounds containing these radicals; *e.g.*, the oxides of chlorine consist of molecules in which two atoms of chlorine are linked to each other by one or more intermediate atoms of oxygen; the formulæ for perchloric oxide, in which there is a chain of such linking atoms of oxygen, are—

$$\left\{\begin{matrix}\mathbf{O}Cl\\O\\O\\\mathbf{O}Cl\end{matrix}\right. \quad \text{Cl—O—O—O—O—Cl}$$

Preparation. This substance can only be procured by an indirect process, that of passing carbonic anhydride through water in which baric peroxide is suspended; the following change takes place if the mixture be kept cool:—

$$\underset{\text{Baric peroxide.}}{\left\{\begin{matrix}\mathbf{O}\\\mathbf{O}\end{matrix}\right.Ba''} + \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Baric carbonate.}}{\mathbf{C}OBao''} + \underset{\text{Hydroxyl.}}{\left\{\begin{matrix}\mathbf{O}H\\\mathbf{O}H.\end{matrix}\right.}$$

The operation is sometimes performed with hydrochloric acid; so that, instead of the insoluble baric carbonate, soluble baric chloride is formed. The subsequent cautious addition of sul-

phuric acid transforms the latter salt into the insoluble sulphate:—

$$\left\{\begin{matrix}\mathbf{O}\\\mathbf{O}\end{matrix}\right\}\mathrm{Ba''} + \mathbf{O}\mathrm{H_2} + 2\mathrm{HCl} = \mathbf{Ba}\mathrm{''Cl_2} + \mathbf{O}\mathrm{H_2} + \left\{\begin{matrix}\mathbf{O}\mathrm{H}\\\mathbf{O}\mathrm{H}.\end{matrix}\right.$$

Baric peroxide. Water. Hydrochloric acid. Baric chloride. Water. Hydroxyl.

$$\mathbf{Ba}\mathrm{''Cl_2} + \mathbf{S}^{\mathrm{vi}}\mathrm{O_2Ho_2} = \mathbf{S}^{\mathrm{vi}}\mathrm{O_2Bao''} + 2\mathrm{HCl}.$$

Baric chloride. Sulphuric acid. Baric sulphate. Hydrochloric acid.

Properties. Hydroxyl is a syrupy, colourless liquid, with an odour resembling that of much-diluted chlorine, and an astringent taste. Its specific gravity is 1·543. At — 30° C. it remains liquid, but at higher temperatures it decomposes, evolving oxygen at about 20° C. At 100° C. it decomposes instantaneously with some violence. It is soluble in water at all temperatures; the solution does not decompose so readily as the pure liquid, especially if a little sulphuric acid be mixed with it.

Hydric peroxide or hydroxyl bleaches litmus and other vegetable colours; it has powerful oxidising properties, affording three different kinds of curious reactions:—

i. Metallic silver, or platinum in powder, by what is called a catalytic action, decomposes it into water and oxygen.

ii. Other bodies decompose hydroxyl, but oxidise themselves at its expense; *e.g.*, black plumbic sulphide ($\mathbf{Pb}$''S) becomes white plumbic sulphate ($\mathbf{S}^{\mathrm{vi}}\mathrm{O_2Pbo''}$); this is turned to account in restoring the colour of oil paintings, in which the white lead has become blackened by exposure to air containing sulphuretted hydrogen.

iii. On argentic oxide (suspended in water) it has a remarkable action, which gives material support to the theory that elementary bodies, such as oxygen, consist, in the free state, of molecules in which two atoms are combined:—

$$\mathbf{O}\mathrm{Ag_2} + \left\{\begin{matrix}\mathbf{O}\mathrm{H}\\\mathbf{O}\mathrm{H}\end{matrix}\right. = \mathrm{Ag_2} + \mathbf{O}\mathrm{H_2} + \mathrm{O_2};$$

Argentic oxide. Hydroxyl. Silver. Water. Oxygen.

for in this reaction the atom of oxygen, released from the hydric peroxide, has the power of depriving the argentic oxide of its oxygen atom, so as to form a molecule of free oxygen.

Uses. Hydric peroxide is practically applied both to the restoration of colours in oil paintings and to medicinal purposes.

Chapter XI.

NITROGEN, *Azote*, N_2.

Atomic Weight = 14. *Molec. Weight* = 28. *Molec. Volume* □□. 1 *litre weighs* 14 *criths. Equivalence* v (*often reduced to* iii, *sometimes to* i).

Occurrence. Nitrogen (nitre; γεννάω, I produce,) or azote (*a*, priv.; ζωή, life), was discovered by Rutherford in 1722, and is the gas which, in admixture with one-fourth its volume of oxygen, constitutes the bulk of our atmosphere. It is therefore one of the most abundant elements. In combination, it is found in the potassic and sodic nitrates, and in ammonia, and also as an essential constituent of the tissues of animals and of many vegetable substances, such as quinine, prussic acid, &c.; but plants, though never entirely devoid of nitrogen, do not possess it as an abundant constituent.

Preparation. 1. The ordinary method of obtaining a small quantity of nitrogen for experimental purposes is to remove the oxygen from a confined body of air by the combustion of phosphorus. The gas which is left is nearly pure nitrogen. The oxygen and phosphorus combine in the following manner to form phosphoric anhydride:—

$$P_4 + 5O_2 = 2P^{v}_2O_5.$$

The mode of proceeding is to place some phosphorus, dried by means of blotting paper, in a porcelain dish floating on the pneumatic trough, and, after igniting it, to invert over it a glass bell-jar or receiver. The water absorbs the white flakes

of phosphoric anhydride formed, and, notwithstanding the elevation of temperature, is forced by the external pressure of the atmosphere to rise in the jar and replace the oxygen.

2. To obtain large quantities of nitrogen, pass air through a tube of hard glass heated to dull redness and filled with finely divided metallic copper (as obtained in the process described at p. 85 for the reduction of cupric oxide). The copper is oxidised at the expense of the atmospheric oxygen, and the nitrogen passes on and may be collected over water. If it be wished to apply this process to the determination of the relative amounts of nitrogen and oxygen present in the atmosphere, the precautions of MM. Dumas and Boussingault described below (p. 121) must be adopted.

3. Oxygen may likewise be removed from air by means of several other substances—*e.g.*, moistened iron filings, lead shavings, and sulphides of the metals—as well as by the slow action of a stick of phosphorus at the ordinary temperature.

All these are processes for obtaining nitrogen from air; but nitrogen may also be obtained by the following decompositions:—

4. Ammonic nitrite heated in a retort yields only nitrogen and water:—

$$\underset{\text{Ammonic nitrite.}}{\mathbf{N}'''\mathrm{O}(\mathrm{N^{v}H_4O})'} = \underset{\text{Water.}}{2\mathbf{O}\mathrm{H_2}} + \mathrm{N_2}.$$

5. Chlorine gas passed into a solution of ammonia at ordinary temperatures produces the following change:—

$$\underset{\text{Ammonia.}}{8\mathbf{N}^{v}\mathrm{H_4Ho}} + \underset{\text{Chlorine.}}{3\mathrm{Cl_2}} = \underset{\text{Ammonic chloride.}}{6\mathbf{N}^{v}\mathrm{H_4Cl}} + \underset{\text{Water.}}{8\mathbf{O}\mathrm{H_2}} + \mathrm{N_2}.$$

Great care must be taken to guard against an excess of chlorine, and to replace the solution constantly by fresh ammonia, otherwise a very dangerous detonating compound—nitrous chloride—is formed.

Properties. Nitrogen is a transparent, colourless, inodorous, and tasteless gas. Its specific gravity is 14 (0·972 air

standard), hence it is a little lighter than air. It is a permanent gas; that is, it has never been liquefied, and contracts so regularly down to −140° (the lowest temperature yet attained) that it does not seem, like some gases, to be at that point, even under the greatest pressure, approaching liquefaction. A hundred volumes of water absorb only about 1·6 volumes of this gas at the ordinary temperature and pressure (15°·5 C. and 760 mm. bar. pressure).

Nitrogen is not poisonous, but will neither support life and combustion—as may be shown by placing in the gas a small animal, or a burning taper which is immediately extinguished—nor will it burn, except at very intensely high temperatures, such as are produced by a jet of hydrogen, by the oxy-hydrogen blow-pipe, or by the electric spark, the brilliancy of which is due to the ignition of the particles of air through which it passes. In these cases compounds of nitrogen and oxygen—such as nitric acid—are formed in small quantities; but the combustion does not spread or cause an explosion in the mixture of these gases, as it would in a mixture of oxygen and hydrogen, because the temperature produced by the combustion is lower than the point of ignition of the mixture, and too low, therefore, for the ignition of the adjacent particles and for the propagation of the combustion. Nitrogen refuses to combine otherwise than indirectly with hydrogen. Nitrogen supports the combustion of three metals, viz., titanium, tantalum, and tungsten, and also of boron. Nitrogen cannot be said to be either basylous or chlorous, as it seems to combine with equally feeble energy with both classes of elements. In contrast with the absence of positive active and remarkable properties in nitrogen itself is the fact that its compounds with oxygen, hydrogen, &c., are characterised by very active and striking qualities.

Use. The great use of nitrogen is that which it serves in our atmosphere by tempering the intensity of the properties of oxygen.

COMPOUND OF HYDROGEN WITH NITROGEN.

Nitrogen and hydrogen do not combine directly. The only compound of these gases which has ever been isolated is ammonia, $N'''H_3$. But in compounds in which other elements (*e.g.*, chlorine) are also present, and the nitrogen atom is pent-equivalent, it has often four atoms of hydrogen combined with it; thus the formula of sal-ammoniac is N^vH_4Cl. This substance and many similar salts are analogous in constitution, as well as in properties, to the salts of the alkali-metals. And, according to Ampère's ammonium theory, the compound N^vH_4 is regarded as a monequivalent basylous radical, incapable of a separate existence, but in its compounds playing the part of a metal analogous to potassium and sodium. Such compounds as sal-ammoniac are therefore called ammonic salts.

AMMONIA, NH_3.

Molecular weight = 17. *Molecular volume* □□. 1 *litre weighs* 8·5 *criths. Fuses at* − 75°. *Boils at* − 38°·5.

Occurrence. The name of this important compound is derived from the fact that the salt from which it was originally obtained was first prepared by Arabs, from camels' dung, near the temple of Jupiter Ammon, in Lybia, and hence termed sal-ammoniac. Owing to its production during the decomposition of animal matters, it is always present in the atmosphere, especially in dry weather, and also dissolved in dew and rain. It plays an important part in the nourishment of plants. It is present in large quantities in guano, the dried excrement of sea-birds, and in the urine of animals.

Preparation. Owing to its great affinity for water, this gas must be collected either over mercury or by upwards displacement of air in inverted dry bottles. But if only a solution be required, the gas is conducted into a series of Woulfe's bottles containing water.

1. The chief part of the ammonia used in England is

obtained from the refuse ammoniacal products afforded in the manufacture of coal-gas. From the ammonic sulphide and carbonate contained in this liquor, ammonic sulphate or chloride is obtained, by means of acids. Dry quicklime (or, if a solution is to be made, slaked lime made into a paste with water) is mixed with either of these salts, and gently heated in a retort, when ammonia is evolved:

$$\underset{\text{Ammonic chloride.}}{2\mathbf{N}^{v}H_4Cl} + \underset{\text{Calcic oxide.}}{\mathbf{Ca}''O} = \underset{\text{Calcic chloride.}}{\mathbf{Ca}''Cl_2} + \underset{\text{Ammonia.}}{2\mathbf{N}'''H_3} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

If dry gas is required, a few lumps of lime should be placed on the surface of the mixture in the retort, so as to retain moisture.

2. Nitrogenised organic matter, such as guano, heated with hydrated alkalies, soda-lime especially, yield all their nitrogen (except that contained in nitrates or cyanides), in combination with hydrogen as ammonia.

3. The destructive distillation of organic matter containing nitrogen in closed vessels affords ammonia. Amongst the products of the distillation of bones are ammonia and ammonic carbonate, and some ammonic chloride, whilst animal charcoal or bone-black remains.

Properties. Ammonia is a colourless and transparent gas, with a pungent and characteristic taste and odour. Since its molecule occupies the same volume as that of hydrogen and its molecular weight is 17, whilst that of hydrogen is 2, its specific gravity is 8·5 (air standard 0·59). A temperature of — 40° reduces this gas to a colourless liquid, which boils at — 38°·5, and freezes at — 75° to a white translucent crystalline solid, which has a higher specific gravity than the liquid. Good boxwood charcoal absorbs in the cold 90 times its bulk of ammonia.

		Litres of NH_3.	Sp. gr. of liquid formed.
At 0°	one litre of water takes up	1050	0·853
„ 15°·4	„ „ „	727	0·886
„ 25°	„ „ „	586	0·900

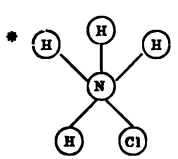
The absorption is accompanied by a considerable rise of temperature. The solution—to which the name of "spirits of hartshorn" used to be given—is colourless and intensely alkaline, has an acrid taste, and blisters the skin when concentrated. At — 40° it freezes, producing a gelatinous inodorous mass; heat drives off the gas ammonia with the appearance of ebullition; nothing but water is left. Ammonia is also highly soluble in alcohol.

When pure this gas is fatal to life, as it produces both an irritating effect upon the lungs, and also spasm of the glottis. When much diluted with water it is a useful stimulant. Ammonia does not support the combustion of bodies which burn in air. Having a high igniting point it will burn only when kept at a high temperature, and then feebly with a pale greenish flame; it is also combustible in pure oxygen. A mixture with an equal volume of oxygen may be detonated by the electric spark; water, nitrogen, and traces of nitric acid are produced. A jet of mixed oxygen and ammonia directed on to a piece of spongy platinum burns with the formation of water and nitric acid:

$$\mathbf{N}'''H_3 + 2O_2 = \mathbf{N}^{v}O_2Ho + \mathbf{O}H_2.$$

Ammonia is powerfully alkaline and renders reddened litmus blue, and turmeric paper brown. Ammonia neutralises the most powerful acids; it forms with them the compounds of pentequivalent nitrogen known as the salts of ammonium. For instance—

$$\underset{}{\mathbf{N}'''H_3} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ammonic chloride.}*}{\mathbf{N}^{v}H_4Cl.}$$



$$\mathbf{N}'''H_3 + \underset{\text{Nitric acid.}}{\mathbf{N}^{v}O_2Ho} = \underset{\text{Ammonic nitrate.}^*}{\mathbf{N}^{v}O_2(N^{v}H_4O)'}.$$

$$2\mathbf{N}'''H_3 + \underset{\text{Sulphuric acid.}}{\mathbf{S}^{vi}O_2Ho_2} = \underset{\text{Ammonic sulphate.}\dagger}{\mathbf{S}^{vi}O_2(N^{v}H_4O)'_2}.$$

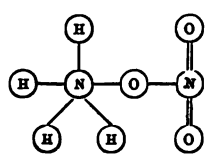
It combines to form these solid compounds when brought into contact with volatile or gaseous acids containing hydrogen; when, for instance, a jar of this gas is brought in contact with a jar of hydrochloric acid gas, white solid ammonic chloride is instantly formed. This property is employed as a test to discover small traces of ammonia; the solution suspected to contain ammonia is mixed with slaked lime or potash and gently heated, whilst a glass rod moistened with hydrochloric acid is held above the mixture; if ammonia be present, white fumes are formed. Ammonia is decomposed by chlorine (v. p. 107), and by bromine, free nitrogen and hydrochloric or hydrobromic acid being formed. With iodine a detonating compound is produced. Sulphur has the following action on ammonia, at a high temperature:—

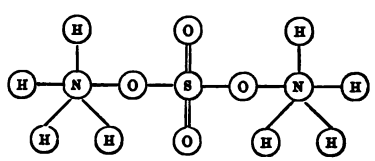
$$10\mathbf{N}'''H_3 + 3S_2 = \underset{\text{Ammonic sulphide.}}{6\mathbf{N}^{v}H_4(HS'')'} + 2N_2.$$

Red-hot charcoal transforms ammonia into ammonic cyanide:

$$2\mathbf{N}'''H_3 + C = \underset{\text{Ammonic cyanide.}}{\mathbf{N}^{v}H_4(CN)'} + H_2.$$

The gas may be resolved into its elements by sparks from a Ruhmkorff's coil, or by passage through a red-hot porcelain tube containing iron or copper turnings heated to dull redness; the gas becomes in either case dilated to twice its volume:

* 

† 

$$2NH_3 = N_2 + 3H_2.$$
4 vols. become 2 + 6 vols.

And then explosion of the mixture with half its volume of oxygen gives the following result:

$$2N_2 + 6H_2 + 4O_2 = 2N_2 + O_2 + 6OH_2.$$
4 + 12 + 8 vols. become 4 + 2 vols. + condensed steam.

Uses. A solution of ammonia is one of the chief re-agents employed in the laboratory. As a stimulant both the solution and the gas are of great value, the former medicinally, the latter in the form of smelling salts, &c. In M. Carré's refrigerating machine the alternate condensation and vaporisation of ammonia has received an interesting practical application.

Chapter XII.

THE EARTH'S ATMOSPHERE.

Evidence of Existence and Weight. That invisible matter exists above the visible crust of our globe is evident from the resistance offered to motion near the earth's surface, and from the effects produced by wind. That air has weight is proved by the fact that a vessel from which air has been removed weighs less than the same vessel filled with air.

Atmospheric Pressure: The Barometer. It follows from the fact that air has weight or obeys the laws of gravitation that it exerts a certain pressure at the earth's surface. To this pressure is due, as Galileo first explained (A.D. 1640), the fact that water cannot be raised more than 9·75 metres (32 feet) by a suction pump. This explanation was conclusively verified by Galileo's pupil Torricelli (A.D. 1643), who argued that, if the atmospheric pressure supports a column of water 9·75 metres (32 feet) in height, it cannot support a column of mercury, a liquid nearly fourteen times heavier than water, of more than about 760 mm. (30 inches) in height. The following is the experiment that he made:—He took a straight glass tube about 800 mm. (33 inches) long, closed at one end, and open at the other; he filled it with mercury, closed the open end with his finger, inverted the tube, and then plunged its extremity into a basin of mercury. When he removed his finger he observed that the column of mercury in the tube fell till its summit was at a height of about 760 mm. (30 inches) above the surface of the mercury in the basin. The vacuum thus formed above the mercury is called the "*Torricellian vacuum.*" If at the top of the closed end of this instrument,

which is simply the common barometer (Fig. 6), a hole is broken, the mercury instantly falls to the level of that in the basin. Now what are the causes of these phenomena? When the tube has been broken and is open at both ends, the atmospheric pressure acts downwards on the mercury in the tube with just the same force as that exerted upwards at the bottom of the tube by the mercury on which the atmosphere is pressing in the basin. Hence the mercury in the tube must seek to remain at the same level as that in the basin. But if, either by means of a pump or by Torricelli's experiment, we contrive that no downwards pressure shall act on the column of mercury in the tube, it is forced up by the pressure exerted on the mercury in the basin, till its own weight is sufficient to counterbalance this pressure—that is, till the weight of the column is equal to the force acting at the orifice of the tube, or equal to the weight of a uniform column of air, the size of the base of which is equal to that of the bore of the tube. Hence, however large the tube, the height of the column of mercury is always about 760 mm. (30 inches), varying only with the variations in the height and weight of the column of air pressing on the mercury; so that, as Pascal first declared and proved (A.D. 1648), the column of mercury supported by the atmospheric pressure diminishes when the barometer is carried up a mountain, and increases when it is taken down a pit or well.

FIG. 6.

Another form of barometer is the beautiful instrument called the "aneroid barometer" (*a*, without; *νηρός*, liquid), the essential part of which is a small round metal box, exhausted of air, and with a thin circularly-fluted lid, any movement of which, caused by variations of the atmospheric pressure, is communicated by a complicated system of levers to an index revolving over a dial.

The average weight of the atmosphere at the level of the sea in our latitudes is that of a column of mercury 760 mm. high; it is therefore equal to a pressure of 103·33 kilogrammes on a square decimetre (nearly 15 lbs. on a square inch, or 27,000,000 tons on a square mile). The pressure on the surface of the body of a man of middle size is upwards of 11 tons.

The height to which the atmosphere extends above the earth's surface is greater at the Equator than at the Poles, owing to the diminished power of the force of gravity at the equator, to the action of centrifugal force, and to the equatorial temperature. That there is a definite limit to the earth's atmosphere is certain. It has been calculated that the atmosphere reaches in a state of sensible density to the mean height of from 40 to 45 miles, a height equal to about $\frac{1}{144}$th of the diameter of our globe; though, in a much rarer state, we believe it to extend to a far greater height. This supposition is supported by the fact that meteorites often become luminous, owing apparently to the heat and consequent combustion produced by the retardation of their motion in contact with air, at a height of 200 miles. If the air's density were uniformly that at the earth's surface, the atmosphere would be only five miles high. Half the total weight of the atmosphere lies within three miles of the earth's surface.

From the law of Boyle and Marriotte—that the volume of a gas is inversely and its density directly as the pressure which it sustains, if the temperature remain constant—as well as from the results of numerous experiments, we are enabled to assert that the density of the atmosphere diminishes in a geometrical ratio, as the height at which we observe it increases in an arithmetical ratio. We find, therefore, that at a height of 5,528 metres (18,136 feet) above the level of the sea the pressure is reduced to half its amount, and the air expanded in consequence to double its original volume; and that at twice this height the pressure is reduced to one quarter of its original amount, and so on.

Atmospheric Temperature: Winds. The temperature of the atmosphere diminishes as the distance from the earth's surface increases. The causes of this regular diminution are twofold: in the first place, the air absorbs only a small portion of the solar heat-rays, so that only those portions of the air which come in contact with the warm surface of our globe are much heated; secondly, air, like all gases, undergoes an increase of latent heat with a consequent loss of temperature on rarefaction. The line of perpetual snow, at which the mean temperature is not higher than 0°, is at the equator very high, about 15,200 feet, much less at the latitude of 60°, viz., about 3,800 feet, and in latitude 75° only 1,016 feet above the sea-level; it varies much with the irregularities of geographical conformation. From 18 to 25 per cent. of the solar heat-rays, and about $6\frac{1}{2}$ per cent. of the rays of light, are said to be absorbed in passing through the atmosphere. According to Clausius about 18 per cent. of the rays of direct sunlight are reflected by the atmosphere as diffused light. According to Biot and Arago the refractive power of the air on rays of light from the sun and other celestial objects is equal to 0·000588; the refractive index from the vacuum into air being, at 0° and 760 mm. pressure, 1·000294.

"Owing to the unequal heating effect which the sun produces on the various portions of the earth's surface, either from general or from local causes, the temperature of the atmosphere varies in every part of the globe, and in the same part undergoes continual change, thus producing the motion of masses of air which we call wind. Winds are invariably caused by the ascent of a heated mass of air, and the motion of a colder mass to fill up the space thus left vacant; the former of these gives rise to currents in the higher regions of the atmosphere, whilst the latter produces the horizontal currents which we observe at the surface of the earth. Winds may either be confined to very narrow limits, as for example the sea and land breezes on every coast, or they may extend over a large portion of the globe, as is the case with the trade

winds. The former are caused by local circumstances depending upon the unequal heat-absorbing and radiating power of the sea and land, whilst the latter depend upon the unequal distribution of temperature throughout the globe, being caused by ths rise of hot air from the equatorial zones, inducing horizontal currents to stream in from the colder polar regions. These polar currents would, if the earth were at at rest, move directly south and north to the equator; but, owing to the earth's axial motion, they pass continually over latitudes having a velocity of rotation greater than that of the current, which therefore acts as a north- or south- east wind."*

Atmospheric Air.

Its Composition. Air consists *essentially* of oxygen diluted with nearly four times its volume of nitrogen, and mixed with about $\frac{1}{2500}$th of its volume of carbonic anhydride (often called "carbonic acid") and a variable amount of aqueous vapour. These are the constituents of air indispensable to animal and vegetable life. Amongst the effects which the admixture of this large quantity of nitrogen produces on the atmospheric oxygen are the following: it diminishes the intensity of combustion, reduces the rate of evaporation, renders the existence of marine animals and plants possible, and contributes to the diffusion of light and prolongation of twilight. If the nitrogen which forms so important a part of our atmosphere were removed, and the atmosphere consisted only of the oxygen now present with it, the rapidity and intensity of combustion would be such that iron fire-grates would take fire and be consumed; whilst the reduced pressure of the atmosphere would give rise to increased rapidity of evaporation, causing frequent and tremendous deluges of rain, and also to a di-

* Prof. Roscoe's article on the Atmosphere, Watts's Dictionary of Chemistry. A large part of this chapter is compiled from the same source.

minished absorption of oxygen such as would not support marine life. That air is, as Dalton first successfully contended, merely a mechanical mixture of these gases and not a compound, the following facts conclusively prove:—

1. The composition by volume of atmospheric air would be quite anomalous if it were a compound gas.

2. Its composition by weight is nearly in the proportion of four atoms of nitrogen to one of oxygen, but neither sufficiently exactly nor sufficiently constantly and invariably to warrant the supposition that it is a compound.

3. Air exhibits the properties of both its chief constituents, and has no single property which would not be predicted of a mixture of nitrogen and oxygen. For example, water in contact with air absorbs each gas in the same proportion as it does when the gas is uncombined; that is, for every volume of nitrogen, about twice as much oxygen.

4. When a mixture of nitrogen and oxygen in the proportions in which they are found in the atmosphere is made, none of the phenomena, such as evolution of heat and alteration of properties and volume, usually attendant on chemical combination, are perceived; and the mixture is actually identical in properties with atmospheric air.

It is no less remarkable than true that, owing to the incessant process of diffusion (v. p. 42) taking place between the gases of which the atmosphere consists, and in spite of the differences in their specific gravities, they are found to be uniformly mixed, in the same proportions, at all heights and latitudes. Local causes only produce slight temporary exceptions to this rule.

That the qualitative composition of the atmosphere is what we have stated it to be, may be proved by the experiment described above (p. 76) as the first mode of preparing oxygen.

The following are methods for the *quantitative* analysis of air:—

I. *Volumetric Processes.*

1. Phosphorus, by its slow action on a measured quantity of air in a jar inverted in the mercurial trough, or by its more rapid action when burned in a confined volume of air in a manner similar to that prescribed as the first mode of preparing nitrogen (p. 106), removes the oxygen. In both cases the nitrogen left at the close of the operation is measured, and the composition of air thus determined.

2. Another and a preferable method of ascertaining the proportion of oxygen in atmospheric air is that of exploding a given volume of air free from carbonic anhydride, in a eudiometer, with half its volume of hydrogen. In lieu of the straight eudiometer described above (p. 84), Dr. Ure's *siphon eudiometer* (Fig. 7) may be used. The air and half its bulk of hydrogen are successively introduced into the vessel over mercury, and transferred to the closed portion of the tube; the mercury is next reduced to the same height in both limbs of the siphon, and the volume of the mixed gases observed; the open end is firmly closed by the thumb, and the electric spark is passed. Finally, when mercury has been added till the level is the same on each side, the volume of the remaining gases must be read off. The following is an example of the method which must be pursued in order to deduce in this manner the proportion of oxygen in air:—

FIG. 7.

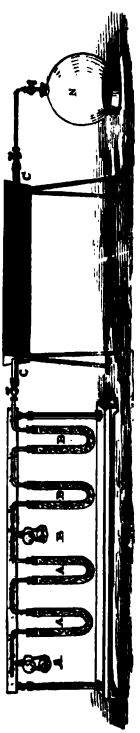
Let the volume of air introduced be.....	100	measures.
The „ hydrogen „ is.....	50	„
Total „ air and hydrogen	150	„
Volume (of N & H) observed after explosion	87	„
Diminution due to O & H	63	„

And, since one volume of oxygen combines with two of hydrogen, $\frac{63}{3} = 21$ is the number expressing the proportion by volume of oxygen in 100 measures of air.

II. *Gravimetric Process.*

This is the method of MM. Dumas and Boussingault; it has this advantage—that in the same experiment the quantity, not only of nitrogen and oxygen, but also of carbonic anhydride and aqueous vapour, present in a given volume of air may be determined. One or more bent tubes—named from their shape U-tubes—are filled either with dry calcic chloride or with pumice-stone, moistened with strong sulphuric acid; to these tubes is attached a piece of apparatus (invented by Liebig) consisting of bulbs filled with a concentrated solution of caustic potash or soda. These U-tubes and bulbs—a double series of which is represented at A and B, in Fig. 8—are connected with a wide porcelain tube C (filled with finely divided copper) which in turn communicates with a large glass globe N. Stopcocks are interposed both between the globe and the porcelain tube, and between the latter and the bulbs and U-tubes. The exhaustion of the glass globe, and its subsequent weighing, as well as the separate weighing of the tube containing the copper, of the U-tubes and their contents, and of the potash bulbs, are necessary preliminaries before these parts of the apparatus may be put together. Secondly, the porcelain tube is heated to redness; then the stopcocks are opened, and air enters the apparatus till the globe is filled. But it is pure nitrogen alone that reaches the globe, for the air loses its aqueous vapour in the U-tubes, and its carbonic anhydride in the potash-bulbs, and is deprived of its oxygen by the heated copper.

FIG. 8.



The respective increase of weight of the several parts of the apparatus on a second weighing will indicate the proportions by weight of aqueous vapour, carbonic anhydride, oxygen, and nitrogen in air. The following is the action which takes place in the potash-bulbs:—

$$\underset{\text{Potash.}}{2OKH} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2} = \underset{\substack{\text{Potassic}\\\text{carbonate.}}}{COK_2O_2} + OH_2.$$

Numerous observations and experiments, conducted according to the plans here described, have ascertained the average composition of the atmosphere in this country to be very nearly as follows:—

AVERAGE COMPOSITION OF THE ATMOSPHERE BY VOLUME.

Nitrogen	77·95
Oxygen	20·61
Aqueous vapour (very variable)	1·40
Carbonic anhydride	·04
Nitric acid, Ammonia, Marsh gas	traces.
Sulphuretted hydrogen (in towns), Sulphurous anhydride („)	traces.

The following is the average percentage composition by weight and by volume of pure and dry air, free from carbonic anhydride:—

	Weight.	Volume.
Nitrogen	76·9	79·1
Oxygen	23·1	20·9

The relative proportions of nitrogen and oxygen in our atmosphere are substantially the same in all parts of the earth. The results of trustworthy analyses to determine the percentage volume of oxygen vary only from 20·85 to 20·999.

The volume of carbonic anhydride in the atmosphere varies from ·03 to ·11 per cent. Even in crowded and ill-ventilated rooms it rarely exceeds ·33 per cent.

The percentage of aqueous vapour in the atmosphere at any given moment, and the "*dewpoint*" of the atmosphere,—or the point of temperature at which, in its particular state of saturation, the air will deposit as dew the aqueous vapour it contains,—are determined by such instruments as Daniell's and Regnault's hygrometers and the wet-bulb thermometer.

"Although the relative amount of 4 volumes of carbonic anhydride in 10,000 volumes of air appears to be a very small one, yet the absolute quantity of carbon thus contained in the atmosphere is very large ..... Whether the atmosphere is now slowly undergoing, or has in past ages undergone, any perceptible change in the amount of its carbonic anhydride, is a question to which, owing to the absence of certain and accurate data, we are as yet unable to give any very satisfactory answer ..... The principal causes which tend to increase the atmospheric carbonic anhydride are:—(1.) The respiration of animals; (2.) Combustion of vegetable carbonised material; (3.) Exhalations of carbonic anhydride, caused by volcanic and other intra-terrestrial agencies .... The causes of diminution consist mainly in: (1.) The decomposition of carbonic anhydride, *i.e.*, reduction of carbon and regeneration of oxygen, which living vegetables effect in sunlight; (2.) The fixation of carbonic anhydride as carbonate of lime by the vital action of certain animalculæ, giving rise to coral reefs and islands, and the whole of the vast limestone deposits; (3.) The fixation of carbonic anhydride by inorganic chemical processes.

"The atmospheric ammonia plays a very important part in vegetation: for it is mainly, if not altogether, from the ammoniacal salts contained in the air that plants obtain the nitrogen which they require for the formation of seed and

other essential parts of their structure. Whether plants are at all able to assimilate the free nitrogen of the atmosphere must, in spite of the numerous researches on the subject, be considered doubtful."*

Properties of Air. Air is, as every one knows, a transparent, colourless, tasteless, and inodorous gas. Its specific gravity, when that of hydrogen is unity, is 14·45; it has, however, been more common, till quite of late, to assume dry and pure air as the unit of specific gravities, and thus to give to hydrogen the specific gravity of 0·0692. The experiments of Regnault assign to a cubic metre of dry air, measured at 0° and 760 mm. bar., a weight of 1·2932 kilogrammes (or to 100 cubic inches of dry air at 0°, and 30·92 inches mercurial pressure a weight of 32·586 grs.). The weights of equal bulks of air and mercury are to each other about as 1 : 11065. Sound travels through air at the rate of about 1,100 feet in a second; its velocity decreases with the temperature, and with anything which tends to make the gas denser. The specific heat of air is 0·237. The solvent effect of water on air has been described.

The chemical properties of the air may be stated to be simply those of very dilute oxygen. Since air is the great supporter of combustion, the subject of combustion may be conveniently noticed at this place.

Combustion. The term combustion is applied to any rapid chemical action between two different substances which is attended with the extrication of light and heat. And of the two substances, one is said to burn, and is called a combustible, whilst the other is a supporter of combustion. These terms are purely conventional. Both substances always burn; and each supports, and is necessary to, the combustion of the other. For instance, a jet of hydrogen burns in an atmosphere of chlorine just as well as a jet of chlorine in an atmosphere of

* Prof. Roscoe's article on the Atmosphere, Watts's Dictionary of Chemistry.

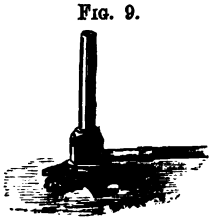
hydrogen; and oxygen or air burns as readily in an atmosphere of hydrogen or coal-gas, as hydrogen or coal-gas in oxygen or air.

That this action between two substances may commence, the absolute contact (v. p. 2) necessary for chemical combination must be insured; to produce this actual contact very different temperatures are needed in the cases of different combustibles. The name *igniting point* is given to that particular temperature at which the atoms of any combustible can be brought into such close relations with those of the supporter of combustion, that combustion commences. The igniting point of carbonic disulphide is so low that a warm glass rod suffices to set up the combustion of this liquid; whilst a mixture of its vapour with atmospheric air may be ignited by the slight rise of temperature developed when the air is subjected to sudden compression. To the comparatively high igniting point of fire-damp, or marsh-gas, is due the fact that the wire gauze of a Davy lamp (v. p. 137) reduces the heat of the flame within sufficiently to prevent its exploding a mixture of fire-damp and air; whereas it could only very imperfectly protect a mixture of coal-gas and air from ignition, and would afford no protection to one of hydrogen and air, since hydrogen and coal-gas have lower igniting points. Some combustibles not only have a high igniting point, but when lit do not produce a temperature as high as the igniting point, or, in other words, sufficiently high to cause the combustion to continue: we have seen that nitrogen is a combustible of this description (p. 108). Some other combustibles burn only with a steady glow, *e.g.*, a diamond in oxygen.

Structure and Properties of Flames. When you light a candle, the following action takes place: the wax or tallow is melted by the combustion of the wick, and is raised through it by capillary attraction; the heat transforms this wax into vapour, which, mixing at this elevated temperature with the air, burns and forms a flame. The flame consists essentially of three parts; the dark core of unburnt vapour within, the

air without, and between the air and the vapour a space filled with mixed air and vapour in the several stages of combination. Two divisions of the latter space may further be distinguished, the innermost and luminous portion, where the combustion is incomplete, and the outer non-luminous shell, in which the combustion of the luminous matter is completed. If the end of a small glass tube is introduced into the dark centre of the flame, the unburnt vapour will pass up the tube, and may be ignited at a distance from the flame. An ordinary gas-flame has a similar constitution, the gas taking the place of the vapour of wax or tallow. In these flames, both of which are instances of the combustion of hydrocarbons, the innermost portion of the space in which the actual combustion is going on is the luminous portion or the flame; this fact is due to the preference of the oxygen of the air for the hydrogen of the combustible; the oxygen of the air removes part of this hydrogen, leaving vapours of denser and more complex hydrocarbons, which become incandescent, or white-hot, and then in turn undergo complete combustion in the outer layer. By bringing down a sheet of paper on the flame, a charred and sooty ring may be obtained, indicating the position of its luminous portion. If the combustion is imperfect, owing to an insufficient supply of oxygen, these dense vapours do not all become oxidised, but some of them escape and condense in the form of soot, and the flame is smoky. If, on the other hand, the supply of oxygen be made more abundant and rapid, by the introduction of air into the internal core of the flame, the combustion is accelerated, the hydrocarbons are more rapidly oxidised, and, whilst the luminosity of the flame is destroyed, its heat is intensified in proportion to the augmented energy of the chemical action. These facts are exemplified, both by the blowpipe flame, and by that of the Bunsen burner, in which (fig. 9) the coal-gas issues from a small central jet, and passing unburnt

FIG. 9.



up a wide tube, draws air up with it through four external holes; at the top of the tube it may be ignited, and burns with a non-luminous, smokeless flame; on closing the holes the flames become bright and smoky. The light of a coal-gas or candle flame is believed to be almost wholly due to the presence of dense vapours, highly ignited; in the absence both of dense vapours and of particles of solid matter a flame is never very luminous, though it may be very hot; as in the case of the flame of the oxy-hydrogen blowpipe, and of hydrogen. But such flames may be made highly luminous, by the introduction of solid matter, or dense vapours; thus, for instance, when the oxy-hydrogen flame is made to impinge on a piece of lime, the intense light invented by Lieutenant Drummond (v. p. 44) is produced; and solid matter, such as powdered charcoal, introduced into the almost invisible flame of hydrogen, renders it luminous. The luminosity of the flames of hydrocarbons used to be explained on the supposition that solid particles of carbon were set free by the action of oxygen on the hydrocarbons, until Dr. Frankland, in a course of lectures on Coal-gas, delivered in March, 1867, at the Royal Institution, proved that this hypothesis was unnecessary, and, arguing from the absence of solid particles in other luminous flames, from the fact that soot and smoke do not consist of pure carbon, but contain a considerable amount of hydrogen, and also from the perfect transparency of the flames in question, proposed the explanation here adopted.

The effects of the condensation or rarefaction of the atmosphere in which a flame burns on its brilliancy, and also on the rate of combustion, are very remarkable and must be briefly noticed. Dr. Frankland's experiments on the summit of Mont Blanc, in August, 1859, resulted in the discovery that at that great elevation, and in so rare an atmosphere, candles burn at a rate almost precisely the same as that observed in the valley of Chamouni under a far greater atmospheric pressure; but the luminosity of the flames was found to be diminished in an extraordinary degree by the elevation.

Six candles were used; but, owing to some defect, one of them gave an abnormal result; the rate of combustion of stearin per hour for each of the other five was as follows:

At Chamouni.....	9·4	grms. per hour.
Summit of Mont Blanc ..	9·2	,,

This slight difference is due to the fact that the temperature at the summit was 21° lower than in the valley, where the stearin was able to melt more readily.

The brilliancy or illuminating effect of flames is greatly affected by increase or decrease of barometric pressure. On the summit of a mountain, or in an artificially rarefied atmosphere, flames lose their luminosity almost entirely. The decrease in illuminating power is found to be very nearly directly proportional to the decrease of barometric pressure. At the bottom of a pit or well, or in condensed air, on the other hand, a flame (*e.g.* that of a spirit-lamp) which is feebly luminous under the normal pressure gives a good light, or even becomes smoky; whilst the flame of an ordinary lamp or candle gives out quantities of smoke, owing to the less complete oxidation of the hydrocarbons.

The explanation of these facts is to be found in the contrast between the great mobility of rare air and the comparative immobility of denser air (v. Phil. Trans. 1861, p. 631). The greater readiness with which the oxygen of the atmosphere finds access to the interior of the flame, owing to the greater mobility of the particles of the air under diminished pressure, accounts—as Dr. Frankland has pointed out—for the decrease in illuminating power. On the other hand, neither the facility with which the tallow is melted, the capillarity of the wick, nor the volatility of bodies possessing such high boiling-points as tallow, wax, &c., is appreciably influenced by the rarity of the atmosphere,—hence the rate of cumbustion of a candle is the same in rarefied air as in air at the normal barometric pressure.

Chapter XIII.

CARBON, C.

Atomic Weight = 12. *Equivalence* iv (*sometimes reduced to* ii).

This very abundant element assumes several distinct forms in the free state, all of which agree in the following

General Properties:—Carbon is always solid. No attempt either to liquefy or to vaporise carbon, or even to dissolve it in any liquid, has ever succeeded.

Each form of carbon will combine at a more or less elevated temperature with oxygen to produce, according to the limited or abundant supply of oxygen, one of two gaseous compounds; carbonic oxide, $\mathbf{C}''O$, — or carbonic anhydride $\mathbf{C}O_2$. Twelve grammes of each kind of carbon combine, when ignited in a free supply of oxygen, to form 44 grms. of carbonic anhydride:

$$C + O_2 = \mathbf{C}O_2.$$

By ignition in a current of hydrogen, carbon may be made to produce acetylene $'''\mathbf{C}'_2H_2$. The compounds of carbon with hydrogen and other elements are so numerous that the study of these substances constitutes by far the larger province of chemical science, viz., "Organic Chemistry," or "the Chemistry of Carbon Compounds." In fact, carbon is the element which enters most essentially into the composition of all the parts both of animals and plants.

Of the inorganic compounds of carbon which occur abundantly in nature, the following are the most notable: carbonic anhydride, a constituent of atmospheric air; many salts of carbonic acid that are minerals of great importance, *e.g.*, chalk,

limestone, marble, and other forms of calcic carbonate, &c., (v. pp. 91, 94).

Allotropic Forms of Carbon. Carbon is found in a state approaching purity in two crystalline forms, viz., the *diamond*, and *graphite*. In an impure condition, associated with organic compounds of carbon, it exists as the amorphous mineral *coal*. Artificially it may be obtained tolerably free from other elements; first, in a crystalline form as graphite,—secondly, as animal and vegetable charcoal,—and thirdly, from coal, in a less pure state, as coke.

THE DIAMOND is found chiefly in India, Borneo, and Brazil. Its source cannot be surmised from the conditions in which it is found; though the fact that intense heat tranforms the diamond into a black substance resembling graphite points to the conclusion that it was not produced by crystallisation after fusion.

Properties. The diamond is transparent and usually colourless, though sometimes tinted. Its hardness is greater than that of any known body, but is approached by that of crystallised boron; hence diamonds can be polished only by means of their own powder, or by pulverised crystals of boron. The crystals of the diamond have forms belonging to the regular system, and frequently convex faces and lenticular or rounded edges. Its specific gravity varies from 3·3 to 3·5. The diamond is a non-conductor of electricity, and has a brilliant lustre and a high refracting power; heated to redness, and introduced into an atmosphere of oxygen, it burns with a steady light, forming carbonic anhydride, and leaving a minute trace of yellowish ash in which iron and silica have been detected.

Uses. The chief practical purpose to which the diamond is applied is the cutting of sheets of glass by means of the natural edges of its crystals. Its extraordinary value as a gem needs only a passing notice.

GRAPHITE OR PLUMBAGO (also known as *black lead*) is found in some of the earliest geological formations, and con-

sists not improbably of the remains of very ancient vegetation. Its most important mines are in Siberia, China, Ceylon, and the United States. The Borrowdale mine in Cumberland is becoming exhausted.

Properties. The leaden-grey metallic lustre of graphite, its friability, the marks it leaves on paper, its specific gravity (2·15 to 2·35), its admirable conductivity for heat and electricity, and the form of its crystals (six-sided plates belonging to the rhombohedral system), are the chief characteristics of this form of carbon. It is never found in a perfectly unmixed condition, so that when burned in oxygen it leaves from two to five per cent. of ash.

Uses. Graphite is used in the manufacture of crucibles for metallurgical operations, and of lead-pencils; also for lubricating machinery and protecting iron surfaces from rust.

Preparation. Artificially the characteristic six-sided plates of graphite may be produced by allowing iron which has been melted with excess of charcoal to cool slowly. A very hard form of graphite, *gas-carbon*, deposited on the hottest parts of the retorts used in the manufacture of coal-gas, and due to its partial decomposition, is employed in Bunsen's galvanic battery as a substitute for the platinum of Grove's battery.

CHARCOAL.—Wood charcoal is obtained either by distilling wood in cast-iron cylinders, when volatile products such as acetic acid (or vinegar) pass over, or by setting on fire great heaps of wood covered over with earth. Animal charcoal or bone-black is prepared by calcining bones in closed vessels.

Properties and Uses. The most remarkable property of this black amorphous form of carbon is its absorptive power on gases and vapours, and on some other substances, especially colouring matters. Wood charcoal condenses into its pores many times its own volume of various gases, especially of those most soluble in water and most readily liquefied. Wood charcoal which has been freed by a red-heat or by exposure in a vacuum from the gases with which it happens to be saturated will absorb in 24 hours about 90 times its volume of

ammonia, 85 volumes of hydrochloric acid, 65 of sulphurous anhydride, 55 of sulphuretted hydrogen, 35 of carbonic anhydride, or 9½ of oxygen. When a bit of charcoal saturated with sulphuretted hydrogen is brought in contact with free oxygen an explosion takes place. Owing in part to this absorptive power on gases, and in part to the power possessed by the oxygen of the air condensed in the pores of the charcoal to burn other gases brought thus closely in contact with it, wood charcoal enjoys remarkable deodorising and disinfecting qualities. Animal charcoal has also these properties of an absorbent and deodoriser of gases, but to a less degree. On the other hand, it is a much better decoloriser of organic substances such as indigo, logwood, &c.—a property rendering it of great importance in the refining of sugar; and filtration through animal charcoal is the best practical method of removing organic impurities from water.

Lamp-black has usually been placed among the forms of carbon; but there are good reasons for believing that it consists altogether of hydrocarbons which do not yield up their hydrogen till they have undergone calcination. The fine powder thus produced is used for the preparation of Indian ink and other black pigments.

Coal.—Whilst there are reasons for the presumption that graphite had its source in the vegetable kingdom, coal affords internal evidence from its structure, and from the fossils it contains, that it consists of the remains of forests and swamps with which portions of our globe were anciently covered. These remains, buried under masses of sandstone and other stratified rocks, and thus subjected to great pressure during the process of decomposition, have undergone changes the various stages of which are observed in *peat*, *lignite* or *brown coal* (the coal of most recent formation which has lost least of its original woody structure), ordinary *pit coal* (including *caking coal*, *cannel*, &c.), *semi-anthracite* and *anthracite*. From beds of brown coal, and throughout the first stages in the production of coal, carbonic anhydride is evolved; this, no

doubt, is the source of much of the free carbonic acid in effervescent natural waters. The later products of decomposition, when from the lignite ordinary pit-coal is being formed, and when in turn the latter is being converted into anthracite, are hydrocarbons, such as marsh-gas or fire-damp, rock-oil, &c. And since these compounds and water, which is simultaneously formed, contain and carry off with them more atoms of oxygen and hydrogen than of carbon, the percentage of atoms of free carbon in the mass is continually on the increase. Thus at length anthracite, of which about 94 per cent. by weight consist of carbon, results from these slow changes; possibly a longer exposure to pressure and to the internal heat of the earth converts anthracite into graphite. Reservoirs of compressed carbonic anhydride (or choke-damp) and fire-damp, due to the decomposition of the vegetable substances during the successive stages of their conversion into coal, pent up in the crevices of seams of pit-coal, give rise to the frequent accidents which occur in mines. Earthy and saline matter is present in all coal, and forms its ash.

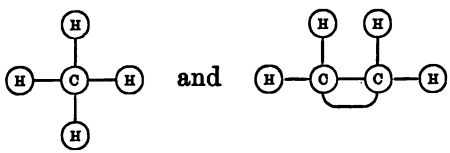
Coke is the substance left when caking-coal is heated in retorts or ovens into which no air is admitted, but from which the volatile products can freely escape. Coke is a fuel more difficult to ignite than coal, but it has many advantages, especially that of producing intense heat with little or no smoke.

COMPOUNDS OF HYDROGEN WITH CARBON.

Of the vast number of compounds called hydrocarbons, in which carbon exists combined either with hydrogen alone or with hydrogen and oxygen, we shall study but two, viz., olefiant gas or ethylene, and marsh-gas or methylic hydride. Both ethylene and methylic hydride belong at least as much to the organic as to the inorganic province of the science; for, though they may be built up from their elements without the aid of vital action, they are never naturally so formed.

The molecule of the latter is represented by the formula CH_4. It is the compound of the monad radical methyl, CH_3, with hydrogen.

Ethylene, $''C''_2H_4$, consists of two atoms of the diequivalent radical $(C^{IV}H_2)''$; hence two bonds of each atom of carbon are employed in holding the two carbon atoms together, thus:—



MARSH GAS or METHYLIC HYDRIDE, CH_4 or MeH.

Molec. Weight = 16. *Sp. Gr.* = 8. *Molec. Vol.* □□. 1 *litre weighs* 8 *crith*s.

Occurrence. This gas, also called *light carburetted hydrogen*, or *fire-damp*, one of the most abundant products of the decomposition of organic matter, especially in the mud of stagnant pools and in peat, is evolved from coal during its later stages of change, and is one of the chief constituents of coal-gas. The mud volcano at Bulganak, in the Crimea, evolves nearly pure marsh-gas.

Preparation. 1. The process possessing the greatest theoretical interest is the decomposition of zincic methide (a compound which may be described as water, in which the oxygen is replaced by the metal zinc, and the hydrogen by the monequivalent radical methyl) by means of water:—

$$\underset{\text{Zincic methide.}}{Zn''(C^{IV}H_3)'_2} + \underset{\text{Water.}}{2HHo} = \underset{\text{Zincic hydrate.}}{Zn''Ho_2} + \underset{\text{Methylic hydride.}}{2CH_4}.$$

2. A much more usual plan is to distil in a copper retort, at a dull red-heat, 2 parts of potassic acetate, with 2 of

potassic hydrate and 3 of lime, the addition of which prevents fusion. Methyl—an essential constituent of acetic acid, $\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OHo\end{matrix}\right.$—abstracts hydrogen from the potash, and the combined residues form potassic carbonate:—

$$\underset{\text{Potassic acetate.}}{\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}OKo\end{matrix}\right.} + KHo = \underset{\text{Potassic carbonate.}}{\mathbf{C}OKo_2} + \mathbf{C}H_4.$$

Baric hydrate may be substituted for the potash, and sodic for potassic acetate:—

$$2\left\{\begin{matrix}\mathbf{C}H_3\\ \mathbf{C}ONao\end{matrix}\right. + \mathbf{Ba}''Ho_2 = \underset{\text{Baric carbonate.}}{\mathbf{C}OBao''} + \underset{\text{Sodic carbonate.}}{\mathbf{C}ONao_2} + 2\mathbf{C}H_4.$$

Sodic acetate.

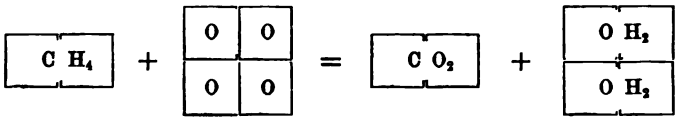
3. The action of nascent hydrogen (produced from alkali by sodium amalgam) either (a.) on carbonic chloride, or (b.) on chloroform:—

$$\text{(a.)}\quad \mathbf{C}Cl_4 + 4H_2 = 4HCl + \mathbf{C}H_4.$$
$$\text{(b.)}\quad \mathbf{C}HCl_3 + 3H_2 = 3HCl + \mathbf{C}H_4.$$

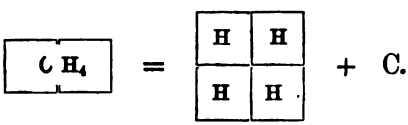
Properties. It is a transparent, colourless, tasteless, and inodorous gas, and has the specific gravity 8, being lighter than any known substance except hydrogen. Marsh-gas has hitherto resisted all attempts to liquefy it. It is a little more soluble than oxygen in water, which dissolves rather more than $\frac{1}{11}$th of its volume of marsh-gas at the normal temperature. Alcohol also dissolves a small quantity.

If diluted with air it is not injurious to life. It does not support combustion, but burns with a bluish-yellow flame, very slightly more luminous than that of hydrogen; if the gas be heated before it reaches the jet, or if the flame be made very large so that the cooling effect of the surrounding air upon it is less, marsh-gas gives more light. For the complete combustion of 2 litres, 4 litres of oxygen are required; such a

mixture on the application of a flame or the passage of the electric spark detonates even more violently than oxy-hydrogen gas:—



Mixed with less than 7, or more than 14, times its volume of air, fire-damp will not explode. The most violent explosion produced by air and marsh-gas is given by a mixture containing 10 volumes of air to every volume of the gas. Chlorine does not act on marsh-gas at all in the dark; the action is slow in diffused daylight, but rapid in sunlight, methylic chloride being formed: $CH_4 + Cl_2 = HCl + CH_3Cl$. When burned in an atmosphere of chlorine, marsh-gas gives a luminous flame with a great deposition of carbon and the formation of hydrochloric acid. A succession of electric sparks—or transmission through a white-hot tube—causes the separation of all the carbon of methylic hydride, whilst hydrogen occupying twice the original volume is set free:—



Since this gas is formed abundantly during the slow production of coal at great depths, it is found in many coal-mines accumulated at a high pressure in reservoirs, whence a violent "blower" is liable to burst forth, when an opening is accidentally made, filling the workings suddenly with an explosive mixture of fire-damp and air. It is a wise precaution in mines where this danger is known to exist, always to keep a bore-hole some yards in advance of the working, so that the stores of gas may be tapped with safety; the blower may either be burnt at the orifice of the bore-hole before air has become

mixed with the gas, or it may be safely applied to the lighting of the mine with the aid of gas-pipes and burners. But it is also essential to the security of the colliers that no unprotected flame or lighted pipe should be permitted in the mine, and that a system of thorough ventilation should exist, capable of speedily removing any fire-damp that may burst forth.

Davy's Safety Lamp (Fig. 10), should always be used in such mines. It is an oil lamp the flame of which is completely covered by a cylinder of fine wire gauze, through which air and the products of combustion can freely pass, but which protects any mixture of fire-damp and air* outside the lamp from ignition by the flame within. A Davy lamp brought into such an explosive mixture becomes filled with a pale mass of flame, and warns the miner to escape before the gauze becomes overheated or oxidised so as to expose the naked flame. The principle of Sir Humphrey Davy's invention may be explained by the following experiments:—Introduce any substance having a high conductivity—a copper wire for instance—into a flame; the metal cools the flame and produces a dark space around itself. You may extinguish a small flame by means of the cooling effect of a coil of wire. A piece of wire gauze brought down on a flame will cut off its upper part, and, though the combustible gases rise through the wire, the flame below will be powerless to ignite them. In like manner, if a piece of wire gauze be held an inch or two above a gas jet, the gas may be ignited above the gauze, but the combustion will not spread to the lower

Fig. 10.

* In a mixture having a lower igniting point—*e.g.* hydrogen and air—the safety-lamp affords no protection; it cannot therefore be introduced without danger into a mixture of ordinary coal-gas, 50 per cent. of which consist of hydrogen, with air.

side of it. In both cases the wires take away so much of the heat that the inflammable gases cannot reach their igniting point.

Uses. Except as a constituent of coal gas, this hydrocarbon has been applied to no practical purpose, save in a few cases when a blower of fire-damp or marsh-gas has been temporarily employed as a source of light or heat.

ETHYLENE or OLEFIANT GAS, $\left\{ \begin{matrix} \text{''}\mathbf{C}\text{''}\mathrm{H}_2 \\ \text{''}\mathbf{C}\text{''}\mathrm{H}_2. \end{matrix} \right.$

Molecular weight = 28. *Sp. gr.* = 14. *Molecular vol.* $\square\square$.
1 *litre weighs* 14 *criths.*

Occurrence. Olefiant gas or *heavy carburetted hydrogen* is an important constituent of coal-gas, but has never been found free in nature.

Preparation. Abstract water from ordinary (or ethylic) alcohol $\left\{ \begin{matrix} \mathbf{C}\mathrm{H}_2\mathrm{H} \\ \mathbf{C}\mathrm{H}_2\mathrm{Ho} \end{matrix} \right.$:

(a.) By means of concentrated sulphuric acid: mix it with about half its bulk of alcohol in a large retort or flask, and distil; pass the gas evolved through some strong sulphuric acid, to remove water, alcohol vapour, and ether, and through bulbs containing potash, which absorbs any sulphurous or carbonic acids formed; sand should be added to the mixture in the retort to diminish its tendency to froth:

$$\underset{\text{Ethylic alcohol.}}{\left\{ \begin{matrix} \text{'}\mathbf{C}\text{'''}\mathrm{H}_3 \\ \text{'}\mathbf{C}\text{'''}\mathrm{H}_2\mathrm{Ho} \end{matrix} \right.} = \underset{\text{Ethylene.}}{\left\{ \begin{matrix} \text{''}\mathbf{C}\text{''}\mathrm{H}_2 \\ \text{''}\mathbf{C}\text{''}\mathrm{H}_2 \end{matrix} \right.} + \mathbf{O}\mathrm{H}_2.$$

(b) By means of phosphoric anhydride, even in the cold, but especially on heating:

$$3 \left\{ \begin{matrix} \mathbf{C}\mathrm{H}_3 \\ \mathbf{C}\mathrm{H}_2\mathrm{Ho} \end{matrix} \right. + \mathbf{P}^{\text{v}}{}_2\mathrm{O}_5 = 3 \left\{ \begin{matrix} \mathbf{C}\mathrm{H}_2 \\ \mathbf{C}\mathrm{H}_2 \end{matrix} \right. + 2\,\mathbf{P}^{\text{v}}\mathrm{OHo}_3.$$

Properties. Ethylene is a colourless gas with a slight

ethereal odour, probably due to the presence of ethereal impurity. Like many other gases formerly thought permanent, it was first liquefied by Dr. Faraday with the aid of great pressure and intense cold. At $-110°$ slight pressure suffices to liquefy it; it has never been frozen. At ordinary temperatures water absorbs about $\frac{1}{12}$ its volume of the gas, and alcohol a good deal more. It is also soluble in oil of turpentine and the fixed oils, and is very readily absorbed by a solution of cuprous chloride.

Ethylene is a non-supporter of life and combustion, but burns in air or oxygen with a white luminous flame. When, owing to the too violent action of the sulphuric acid on the alcohol used in the first process (a), much carbonic oxide is present, the luminosity of the flame is reduced. By passage through a red-hot tube, the gas is decomposed, with deposition of carbon and liberation of methylic hydride, or—at very high temperatures—of hydrogen:

$$\left\{\begin{matrix}\mathbf{C}H_2\\ \mathbf{C}H_2\end{matrix}\right. = \mathbf{C}H_4 + C = C_2 + 2H_2.$$

One volume of this gas mixed with three volumes of oxygen detonates violently when ignited, and undergoes the following change:

$$\boxed{C_2H_4} + \begin{array}{|c|c|c|}\hline O & O & O\\ \hline O & O & O\\ \hline\end{array} = \begin{array}{|c|}\hline C\ O_2\\ \hline C\ O_2\\ \hline\end{array} + \begin{array}{|c|}\hline O\ H_2\\ \hline O\ H_2\\ \hline\end{array}$$

Ethylene and chlorine gases mixed in equal volumes over water combine together in diffused daylight, forming a heavy oily liquid, ethylenic dichloride or *Dutch liquid;* hence the name of *olefiant* gas (*oleum*, oil; *fio*, I become). Such a mixture of equal volumes of ethylene and chlorine sometimes explodes when exposed to direct sunlight:

$$\left\{\begin{matrix}\mathbf{C}H_2\\ \mathbf{C}H_2\end{matrix}\right. + Cl_2 = \left\{\begin{matrix}\mathbf{C}H_2Cl\\ \mathbf{C}H_2Cl\end{matrix}\right.$$

A mixture of one measure of ethylene with two of chlorine burns quietly when kindled, and the whole of the carbon is deposited as a dense smoke; also a jet of ethylene will burn in an atmosphere of chlorine with the deposition of all its carbon:

$$C_2H_4 + 2Cl_2 = C_2 + 4HCl.$$

With sulphuric anhydride ethylene forms a peculiar compound; hence it is completely absorbed by fuming sulphuric acid, and is somewhat soluble in the ordinary acid. It is absorbed by antimonic chloride. As a diad organic radical, the atom of ethylene—$C^{IV}H_2$—enters into and exists in many important combinations.

Use. This gas contributes in a most important degree to the luminosity of coal-gas.

Chapter XIV.

MONADS. SECTION 2.

CHLORINE, BROMINE, IODINE, and FLUORINE.

The compounds which have now come under our notice, especially the four represented by the formulæ, HCl, $-\mathbf{O}H_2$, $-\mathbf{N}H_3$ and $\mathbf{C}H_4$, are examples of combinations of the very simplest nature. Their structure is typical of that of so many chemical compounds, that some chemists consider that the constitution of all compounds whatever may be best explained by *typical formulæ* intended to bring into prominence the points of resemblance between them and some one or more of these types. Unfortunately such formulæ frequently fail to point out some of the most interesting and important relations between the constituent parts of a compound; indeed in some cases, in the forms in which they are ordinarily employed,* they are liable to give erroneous impressions as to the structure of compound molecules. It would, however, be most unwise to lose sight of the theory of *types;* and the student will find it useful to compare with the four typical compounds above cited, and two others ($\mathbf{N}^{v}H_4Cl$ and $\mathbf{S}^{vi}O_2Cl_2$), many groups of substances built up on similar plans.

The elements which form the subject of this chapter are frequently distinguished as the *halogens* (ἅλς, salt, γεννάω, I produce), as by their simple combination with metals they form salts, whilst their compounds with hydrogen are acids.

A remarkable resemblance and a certain gradation in properties is noticeable in this group; at the normal temperature

* The so-called *double* (and *treble*, &c.) *types* are particularly objectionable, and are apt altogether to mislead students.

chlorine is a transparent gas, bromine a scarcely translucent fluid, and iodine an opaque solid; the specific gravity of liquid chlorine is 1·33, of bromine 2·97, and of iodine 4·95; whilst the atomic weight and the vapour density of bromine are nearly the mean of those of chlorine and iodine: $\frac{35{\cdot}5 + 127}{2} = 81{\cdot}25$.*

BROMINE, Br_2.

Atomic weight = 80. *Molec. weight* = 160. *Molec. vol.* □□. *Sp. gr. of vapour*, 80. 1 *litre of vapour weighs* 80 *criths*. *Sp. gr.* 2·966 *at* 15°·5. *Boiling point*, 63°. *Fusing point*, −20°. *Equivalence*, i, (*perhaps* iii. *See note*, p. 68.)

Occurrence. Magnesic bromide, a compound of bromine (βρῶμος, a stench) with magnesium, is found in sea-water, in some mineral waters, and abundantly in the Dead Sea. A silver ore containing bromine is also known.

Preparation. *Bittern*, the mother-liquor which remains when sea water is evaporated till most of its salts have crystallised out, subjected to a current of chlorine, assumes a yellow colour due to free bromine.

$$\underset{\text{Magnesic bromide.}}{\mathbf{Mg}''Br_2} + Cl_2 = \underset{\text{Magnesic chloride.}}{\mathbf{Mg}''Cl_2} + Br_2.$$

Agitation with ether—in which bromine is more soluble than in the saline solution—causes the separation of a golden-yellow ethereal liquid; this must be treated with solution of potash or soda, which abstracts the bromine from the ether.

$$\underset{\text{Potash.}}{6\mathbf{O}KH} + 3Br_2 = \underset{\text{Potassic bromate.}}{\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Ko\end{matrix}\right.} + \underset{\text{Potassic bromide.}}{5KBr} + 3\mathbf{O}H_2.$$

The potassic or sodic bromate and bromide are gently

* Roscoe's Lessons in Elementary Chemistry, p. 106.

ignited after evaporation; the bromate is thus converted into bromide (like chlorate into chloride, p. 77) which is treated just like sodic chloride in the preparation of chlorine; the red bromine vapours are condensed in a receiver containing water cooled by ice:

$$\underset{\text{Potassic bromide.}}{2KBr} + \underset{\text{Manganic oxide.}}{\mathbf{Mn}^{iv}O_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}^{vi}O_2H_{o_2}} = \underset{\text{Potassic sulphate.}}{\mathbf{S}^{vi}O_2K_{o_2}} +$$

$$\underset{\text{Manganous sulphate.}}{\mathbf{S}^{vi}O_2Mno''} + \underset{\text{Water.}}{2\mathbf{O}H_2} + Br_2.$$

Properties. This deep-red, nearly opaque, heavy liquid (probably the only element besides mercury liquid at ordinary temperatures) is very volatile, and emits dense red irritating vapours resembling chlorine in odour. It freezes at — 20° to a crystalline solid. It is a non-conductor of electricity, and a bad conductor of heat. Bromine is slightly soluble in water, rendering it yellow, more soluble in alcohol, and abundantly in ether.

Bromine vapour is irrespirable and unable to support the flame of a taper, nor can bromine vapour and hydrogen be made to combine with explosion. Bromine bleaches many vegetable colours, but with less energy than chlorine, and stains the skin yellow. It is a powerfully irritating poison when swallowed. With organic substances it forms many bromides, and some very interesting compounds. Many metals unite energetically with bromine. Antimony and arsenic burn in its vapour with brilliancy. Argentic bromide is useful in photography.

IODINE, I_2.

Atomic weight = 127, *Molec. weight* = 254. *Molec. vol.* □□. *Sp. gr. of vapour*, 127. 1 *litre of vapour weighs* 127 *criths*. *Sp. gr.* 4·95. *Fusing point*, 107°. *Boiling point*, 180°. *Equivalence* i (*perhaps* iii. *See note p.* 68).

Iodine is found in the tissues of sea-weeds, sponges, and

other forms of marine life,—and in sea-water, one or two rare ores, and some mineral springs.

Preparation. *Kelp*, the ash of marine plants, is treated with boiling water, which dissolves about one-half; all crystallisable salts are removed by evaporation; and to the mother-liquor or *iodine ley*—in which potassic and sodic iodides, and sodic sulphide and hyposulphite, and some sodic carbonate remain—sulphuric acid is added. On allowing the liquid to stand for 24 hours, carbonic and sulphurous anhydrides and sulphuretted hydrogen escape, whilst sodic sulphate mixed with sulphur crystallises out. The remaining liquid is subjected to heat, with various precautions, in a leaden or stoneware retort, manganic oxide being added. The iodine distils over, is condensed in a series of globular receivers, and is finally purified by a second sublimation:—

$$\underset{\text{Potassic iodide.}}{2KI} + Mn^{iv}O_2 + \underset{\text{Sulphuric acid.}}{2S^{vi}O_2Ho_2} = \underset{\text{Potassic suphate.}}{S^{vi}O_2Ko_2} + \underset{\text{Manganous sulphate.}}{S^{vi}O_2Mno''} + \underset{\text{Water.}}{2OH_2} + I_2.$$

Properties. The bluish black scales thus obtained are lustrous like graphite; they stain the skin yellowish-brown; their crystalline form is an octohedron with a rhombic base. At ordinary temperatures iodine is sensibly volatile, and has a faint odour, not unlike that of chlorine. It fuses at 107°, forming a deep brown liquid; its vapour is of a magnificent violet colour (hence the name, *ἰώδης*, violet-coloured). Iodine is scarcely soluble in water, rendering it pale brown, but freely soluble in alcohol, ether, &c., giving brown solutions, and in carbonic disulphide and chloroform, which it renders violet. It is a non-conductor of electricity.

Iodine acts as an irritant poison, but in small quantities is used as a medicine to reduce glandular swellings, &c. Iodine is incombustible in air, has only very trifling bleaching properties, forms iodides with the metals, and combines with

nearly all the substances with which chlorine and bromine combine directly, but usually with less energy.

Free iodine gives to starch an intense blue colour, a most delicate test for iodine. A drop of chlorine water added to a mixture of the solution of an iodide with starch liberates, by the following substitution, enough iodine to give the characteristic colour, which disappears when heated to below 100°, but reappears on cooling: $2KI + Cl_2 = 2KCl + I_2$. Bromine also liberates iodine from its compounds.

FLUORINE, F_2.

Atomic Weight = 19. *Molec. Weight* = 38 (*probably*). *Molec. vol.* □□. *Equivalence* i.

Fluor-spar or calcic fluoride ($\mathbf{Ca}''F_2$) and cryolite ($6NaF, {}'\mathbf{Al}'''_2F_6$) are the only substances in which this element is abundantly found. The bones, and especially the teeth, of animals contain minute quantities of fluorine. This element has perhaps never been obtained, and certainly has not been satisfactorily examined, in the free state; for as soon as it is liberated it attacks and combines with glass and almost every substance with which we are acquainted. No oxide of fluorine is known. Its compounds are closely analogous to those of chlorine, bromine, and iodine.

HYDRIDES OF BROMINE, IODINE, AND FLUORINE.

HYDROBROMIC ACID, HBr.

Molec. weight = 81. *Molec. vol.* □□. 1 *litre weighs* 40·5 *criths. Fusing point* — 73°. *Boiling point* — 69°.

Preparation. 1. Pass mixed bromine vapour and hydrogen through a red-hot tube, or burn hydrogen in a mixture of bromine vapour and air:—

$$H_2 + Br_2 = 2HBr.$$

2. The decomposition of potassic bromide by heating it with phosphoric acid yields hydrobromic acid:—

$$3KBr + \underset{\text{Phosphoric acid.}}{P^{v}OH_3} = \underset{\text{Potassic phosphate.}}{P^{v}OK_3} + 3HBr.$$

3. The action of moisture and gentle heat on phosphorous tribromide results in the following reaction:—

$$\underset{\substack{\text{Phosphorous}\\\text{tribromide.}}}{P'''Br_3} + 3OH_2 = \underset{\text{Phosphorous acid.}}{P^{v}OHH_2} + 3HBr.$$

The gas must be collected over mercury.

Properties. A colourless, irritating, very soluble, liquefiable, solidifiable, and uninflammable gas. It extinguishes flame, and forms, with water, a colourless, fuming solution, denser than that of hydrochloric acid. Chlorine decomposes it thus:

$$2HBr + Cl_2 = 2HCl + Br_2.$$

Its action on metallic oxides is analogous to that of hydrochloric acid:—

$$OKH + HBr = OH_2 + KBr.$$

HYDRIODIC ACID, HI.

Molec. weight = 128. *Molec. vol.* □□. 1 *litre weighs* 64 *criths. Fusing point* — 55°.

Preparation. 1. *By synthesis.* When iodine is heated in hydrogen the volume of the gas becomes doubled; mixed iodine vapour and hydrogen combine in passing through a red-hot tube, or over spongy platinum gently warmed:—

$$H_2 + I_2 = 2HI.$$

2. Place 10 parts of potassic iodide, 5 of water, and 20 of iodine, in a small retort; add cautiously, 1 part of phosphorus

in small fragments; apply a gentle heat; and collect the gas evolved—by downward displacement in dry bottles:—

$$\underset{\text{Potassic iodide.}}{4KI} + 5I_2 + P_2 + 8OH_2 = \underset{\text{Hydric dipotassic phosphate.}}{2P^{v}OHoKo_2} + 14HI.$$

Properties. A colourless, irritating, fuming, liquefiable, solidifiable, and very soluble gas, which neither burns nor supports combustion. A colourless fuming solution may be obtained by transmitting sulphuretted hydrogen through water in which iodine is suspended, and, when the colour of the iodine disappears, decanting from the precipitated sulphur:—

$$2S''H_2 + 2I_2 = S_2 + 4HI.$$

Hydriodic acid is decomposed instantly by chlorine, almost as rapidly by bromine ($2HI + Br_2 = 2HBr + I_2$), or by nitric, nitrous, and sulphuric acids, and slowly by air, the action being assisted by light ($4HI + O_2 = 2OH_2 + 2I_2$). It dissolves many of the metals—*e.g.*, mercury, zinc, and iron—with evolution of hydrogen:—

$$Zn + 2HI = \underset{\text{Zincic iodide.}}{Zn''I_2} + H_2.$$

It converts metallic oxides, hydrates, and some salts including even argentic chloride, into iodides:—

$$AgCl + HI = AgI + HCl.$$

HYDROFLUORIC ACID, HF.

Molec. weight = 20. *Molec. vol.* ☐☐. 1 *litre weighs* 10 *criths.*

Preparation. Heat gently a mixture of pure fluor-spar with two or three times its weight of sulphuric acid:—

$$\underset{\text{Calcic fluoride.}}{Ca''F_2} + S^{vi}O_2Ho_2 = \underset{\text{Calcic sulphate.}}{S^{vi}O_2Cao''} + 2HF.$$

The powerfully corrosive action of the vapour on glass necessitates great care and the employment of a leaden or platinum still. The acid carries off with it from the sulphuric acid some water, which may be removed by means of phosphoric anhydride. It may then be obtained in the liquid state in a receiver kept cool by immersion in a mixture of ice and salt.

Properties. When anhydrous: a colourless, highly irritating, densely fuming gas, which neither burns nor supports combustion, has but little action on perfectly dry glass, and is completely condensed by water. The acid obtained as above is, before treatment with phosphoric anhydride, a colourless, very volatile, densely fuming liquid, which boils at 15°, and remains unfrozen at — 20°; a drop on the skin produces a deep and serious burn. With water it combines with a hissing noise and great development of heat. It is usually preserved in a diluted state in gutta-percha bottles. The metals, except platinum and its allies, and gold, silver, mercury, and lead, dissolve in it with extrication of hydrogen—potassium with an explosion. By mere contact with silica or with a silicate—such as glass—it forms a volatile silicic fluoride: $Si^{iv}O_2 + 4HF = Si^{iv}F_4 + 2OH_2$. Hydrofluoric acid is employed to etch the graduations on thermometers, eudiometers, &c. They are first coated with a thin layer of beeswax; in this the graduations are marked so as to expose lines on the surface of the glass, and these are submitted to the action of the vapour or solution of this acid.

Chapter XV.

ARTIADS. SECTION 1.

OXYGEN, SULPHUR, SELENIUM, and TELLURIUM.

These chlorous elements form a natural group whose hydrogen compounds ($\mathbf{O}H_2$, $\mathbf{S}H_2$, $\mathbf{Se}H_2$, and $\mathbf{Te}H_2$) have analogous properties. Sulphur, selenium, and tellurium exhibit in their atomic weights, specific gravities, and boiling and melting points a gradation similar to that which characterises chlorine, bromine, and iodine.*

Oxygen appears to be invariably a diad; but the other three members of the group are hexads, which, however, frequently possess the *active* equivalence of diads or tetrads only (v. p. 62).

SULPHUR, S_2.

Atomic Weight = 32. *Molec. weight* = 64. *Molec. vol.* □□ *at* 1000° (*but only one-third of this at its boiling-point*). 1 *litre of vapour weighs* 32 *criths. Vap. sp. gr., at* 1000°, 32. *Equivalence* ii, iv, and vi.

Occurrence. Sulphur is an abundant mineral in volcanic districts, especially in Sicily and Iceland. In combination it is widely distributed in the form of sulphides of iron (iron pyrites $\mathbf{Fe}S_2$), copper (copper pyrites), lead (galena $\mathbf{Pb}S$), and zinc (blende $\mathbf{Zn}S$), and sulphates of calcium

* Roscoe's Lessons in Elementary Chemistry, p. 124.

(gypsum), magnesium, barium, strontium, sodium, &c. Sulphur is also one of the constituents of the muscular tissue of animals.

Extraction. When it is mixed with much earthy impurity the mineral is roughly distilled in earthenware retorts, placed in a furnace and connected with earthenware receivers. A second distillation in iron retorts from which the vapour is conducted into large chambers of brickwork—where it is condensed in powder as "flowers of sulphur" and either collected in that state or melted and run off into cylindrical wooden moulds to form "roll sulphur"—fits the sulphur for use in the arts. Sulphur is also obtained by distilling iron or copper pyrites.

Properties. Sulphur is remarkable for the number of allotropic forms in which it may be obtained; of these the following are the chief:—

Condition.	Specific Gravity.	Behaviour with Carbonic Disulphide.
i. Octohedral, amber-yellow ...	2·05	Soluble.
ii. Prismatic, brownish-yellow..	1·98	Transformed into i.
iii. Plastic, pale to deep yellow..	1·95	Insoluble.
iv. Pulverulent, yellow or orange	1·95	Insoluble.

i. Native sulphur is found either in amorphous masses or in form i. Octohedral sulphur may be produced by slowly evaporating a solution of sulphur in carbonic disulphide. The semi-transparent crystals left do not change in the air. They fuse at 115°.

ii. The second variety is obtained when melted sulphur solidifies,—in the formation of roll-sulphur for example. If, after the crust has appeared on the surface of a mass of melted sulphur, it be pierced by a wire,—on pouring out the liquid portion transparent brownish-yellow needles, which fuse, according to Sir B. Brodie, at 120°, will be left. They are not permanent in the air, but soon lose their transparency and

become converted with elevation of temperature into a crumbling mass of minute octohedra. This conversion also takes place rapidly when prisms of sulphur are simply immersed in carbonic disulphide. But an octohedron of sulphur, heated slowly in any other liquid to about 105°, is transformed into a mass of small prismatic crystals.

iii. When sulphur melts it becomes a transparent, limpid, pale-yellow liquid: above 138° it turns brown, and at about 175° almost black: it becomes more and more viscid and treacly, whilst much heat is rendered latent; till at about 250° it is opaque, and cannot on account of its viscidity be poured into another vessel. At about 260° the sulphur becomes again liquid, although not so limpid as it was at 120°; and if it be now poured into cold water the third modification, consisting of soft, elastic threads, varying in colour from pale amber to deep brown, is formed. In a few hours (or suddenly at 100°) it returns for the most part to the octohedral, brittle form, with extrication of latent heat.

iv. Pulverulent, amorphous, and electro-positive sulphur is yellow or orange-coloured, and is obtained when sulphur is removed from its compounds with such chlorous elements as oxygen, bromine, and chlorine. A temperature of 110° slowly transforms it into the octohedral variety; during the process heat is disengaged.

Roll sulphur is nearly opaque, brittle, yellow, and tasteless, and has a slight odour. A roll of sulphur grasped with a warm hand crackles, and often breaks up; this is due to the expansion of the exterior before the heat has warmed the whole mass, for sulphur is a very bad conductor of heat; it also conducts electricity badly, and becomes negatively electric when rubbed with flannel or silk. It melts at about 115°, and, in closed vessels, boils at about 440°, when it gives a deep yellow vapour and may be distilled. Sulphur is insoluble in water. The crystals of forms i and ii are soluble in carbonic disulphide, in disulphurous dichloride— $\left\{\begin{matrix}\mathbf{S}\mathrm{Cl}\\ \mathbf{S}\mathrm{Cl}\end{matrix}\right.$, in benzol, and in boiling oil

of turpentine. All the varieties are somewhat soluble in boiling anhydrous alcohol.

Sulphur is readily inflammable, and takes fire when heated in air to between 230° to 260°, burning with a blue flame, and producing the suffocating odour of sulphurous anhydride, $\mathbf{S}^{iv}O_2$. Finely-divided copper, iron, and silver burn in sulphur vapour with great intensity. With most of the metals, and also with bromine, chlorine, and iodine, this element combines readily. Sulphur dissolves in a solution of potassic hydrate with the formation of potassic sulphide and hyposulphite :—

$$6\mathbf{O}KH + 2S_2 = 2\mathbf{S}''K_2 + \mathbf{S}^{vi}S''OKo_2 + 3\mathbf{O}H_2.$$

Potassic sulphide. Potassic hyposulphite.

Its compounds with basylous elements are called *sulphides;* in them sulphur is almost always a diad only; they correspond closely in composition with the oxides.

Uses. Sulphur is extensively consumed in the manufacture of matches and of gunpowder, and still more in that of sulphuric acid. It is also useful as a medicine in some skin diseases, and in protecting the hop, the vine and other plants from insects, &c.

SELENIUM, Se_2.

Atomic weight = 79. *Molec. weight* = 158. *Molec. vol.* □□. 1 *litre of vapour weighs* 79 *criths. Vap. sp. gr.* 79. *Equivalence* ii, iv, and vi.

Occurrence. Selenides of iron, copper, silver, &c., are found with mineral sulphides, rarely.

Properties. Selenium is obtained in three forms: i. A red amorphous powder, fusing a little above 100°; ii. Vitreous, brittle, deep-brown, with metallic lustre, without taste or smell, insoluble in water, soluble in carbonic disulphide and in oil of vitriol, a non-conductor of heat and electricity; this form becomes plastic above 100°; iii. Crystalline rhomboidal

prisms which melt at 217°, and are obtained from the solution in carbonic disulphide. Selenium boils at about 700°, giving a deep-yellow vapour.

It is not readily inflammable when heated in the air, and burns with a bright blue flame, forming selenious anhydride, which has a disagreeable odour: $Se_2 + 2O_2 = 2\mathbf{Se}^{iv}O_2$.

TELLURIUM, Te_2.

Atomic weight = 128. *Probable molec. weight* = 256. *Sp. gr.* 6·2. *Fuses at* 490° *to* 500°. *Equivalence* ii, iv, and vi.

Occurrence. A rare element, found in Hungarian and Transylvanian mines, chiefly combined with gold, silver, and other metals.

Properties. Tellurium has a bright white metallic lustre, forms a yellow vapour, conducts heat and electricity badly, and burns with a bluish-green flame when heated strongly in air, producing white fumes of tellurous anhydride.

COMPOUNDS OF THE GROUP WITH HYDROGEN.

The most important of these are, water, $\mathbf{O}H_2$, and its analogues, viz.:

Sulphuretted hydrogen or hydrosulphuric acid..... $\mathbf{S}''H_2$.
Seleniuretted hydrogen or hydroselenic acid ..... $\mathbf{Se}''H_2$.
Telluretted hydrogen or hydrotelluric acid..... $\mathbf{Te}''H_2$.

Hydrosulphyl, $'\mathbf{S}'_2H_2$ or Hs_2, is analogous in functions, as well as in structure, to hydroxyl, $\mathbf{O}_2H_2$ or Ho_2. As hydrates may be conveniently represented by such formulæ as $\mathbf{Mg}Ho_2$—so sulphhydrates, *e.g.*, $\mathbf{Mg}(S''H)'_2$, or $\mathbf{Mg}Hs_2$, the corresponding sulphur-compounds, may be regarded as containing one or more atoms of hydrosulphyl.

SULPHURETTED HYDROGEN, *Hydrosulphuric Acid.*

$\mathbf{S}''H_2$.

Molec. weight = 34. *Molec. vol.* [ ][ ]. 1 *litre weighs* 17 *criths. Sp. gr.* 17.

Occurrence. This gas is evolved from volcanoes. It is a product of the decomposition of many animal matters, such as white of eggs; it is found in hepatic mineral waters, and also in waters where decaying organic matter is becoming oxidised at the expense of soluble sulphates, whilst the sulphides formed are decomposed by dissolved carbonic (or other) acid:—

$$\underset{\text{Calcic sulphate.}}{\mathbf{S}^{vi}O_2Cao''} - 2O_2 = \underset{\text{Calcic sulphide.}}{\mathbf{Ca}''S}.$$

$$\mathbf{Ca}S + \underset{\text{Carbonic acid.}}{\mathbf{C}OHo_2} = \underset{\text{Calcic carbonate.}}{\mathbf{C}OCao''} + \mathbf{S}H_2.$$

This takes place in the sea-water on the shores of the west coast of Africa to such a degree that the air is poisoned with sulphuretted hydrogen.

Preparation. 1. By synthesis: on heating sulphur in hydrogen—

$$2H_2 + S_2 = 2\mathbf{S}H_2.$$

2. *The Ordinary Method.* A few pieces of ferrous sulphide are placed in a bottle provided with a funnel through which some dilute sulphuric acid is introduced; the gas is liberated without the aid of heat and is made to pass through a small wash bottle in which is a little water, intended to arrest suspended particles of sulphuric acid, &c., and may be collected over warm water. The action is accompanied by a considerable rise of temperature. Hydrochloric may be substituted for sulphuric acid:

$$\underset{\text{Ferrous sulphide.}}{\mathbf{Fe}''S} + \mathbf{S}^{vi}O_2Ho_2 = \underset{\text{Ferrous sulphate.}}{\mathbf{S}^{vi}O_2Fe\mathbf{o}''} + \mathbf{S}H_2.$$

$$\underset{\text{Ferrous sulphide.}}{\mathbf{Fe}''S} + 2HCl = \underset{\text{Ferrous chloride.}}{\mathbf{Fe}''Cl_2} + \mathbf{S}H_2.$$

3. To obtain *pure* sulphuretted hydrogen, dissolve some lumps of antimonious sulphide in strong hydrochloric acid, warming the mixture gently:

$$\underset{\text{Antimonious sulphide.}}{\mathbf{Sb}'''_2S_3} + 6HCl = \underset{\text{Antimonious chloride.}}{2\mathbf{Sb}'''Cl_3} + 3\mathbf{S}H_2.$$

The latter process has this advantage, that the gas ceases to come off as soon as the source of heat is removed.

Properties. This transparent colourless gas has the odour (especially disgusting when largely diluted with air) of rotten eggs. At 10° under a pressure of 17 atmospheres, or at −74° under the normal pressure, it is reduced to a colourless mobile liquid which boils at −62°, and at −85°·5 forms a transparent solid. Water dissolves at 0° 4·37, and at 15° 3·23 times its bulk of sulphuretted hydrogen; the solution has the smell and taste of the gas, is feebly acid, and is decomposed by the action of the air with deposition of sulphur:

$$2\mathbf{S}H_2 + O_2 = 2\mathbf{O}H_2 + S_2.$$

Even when much diluted with air, this gas is highly poisonous; a good deal less than 1 per cent. in air soon suffices to kill small animals, especially birds. In laboratories it is very desirable that there should be well ventilated cupboards in which the preparation of this offensive gas may be carried on. Since hydrogen has a greater affinity for atmospheric oxygen than for sulphur, sulphuretted hydrogen is a combustible; it burns with a pale blue flame producing sulphurous anhydride. A mixture of sulphuretted hydrogen with half its volume of oxygen may be exploded with deposition of sulphur; but if two volumes of the gas be mixed with

three of oxygen and exploded, sulphurous anhydride is formed; $2\,\mathbf{S}''H_2 + 3O_2 = 2\,\mathbf{O}H_2 + 2\,\mathbf{S}^{iv}O_2$. Sulphuretted hydrogen when passed through a red-hot tube is partly decomposed. On heating a piece of tin in a measured volume of the gas, an equal volume of hydrogen is left, whilst the tin is converted into stannous sulphide. Chlorine has the following action: $2\,\mathbf{S}H_2 + 2\,Cl_2 = 4\,HCl + S_2$. Hence chlorine is an excellent deodoriser for decomposing this gas with the formation of comparatively harmless products. Bromine and iodine exert a similar action. Many metallic compounds rich in oxygen readily break up sulphuretted hydrogen, separating sulphur, whilst water and a sulphide are obtained, *e.g.*:

$$\underset{\text{Ferric oxide.}}{2'\mathbf{Fe}'''_2O_3} + 6\mathbf{S}H_2 = \underset{\text{Ferrous sulphide.}}{4\mathbf{Fe}''S} + 6\mathbf{O}H_2 + S_2.$$

Sulphur-compounds of the metals corresponding to oxides and hydrates—viz., sulphides and sulphhydrates—result from the action of hydrosulphuric acid on the oxides and hydrates (and also on many salts) thus:

$$\underset{\text{Argentic oxide.}}{\mathbf{O}Ag_2} + \mathbf{S}H_2 = \underset{\text{Argentic sulphide.}}{\mathbf{S}''Ag_2} + \mathbf{O}H_2.$$

$$\underset{\text{Plumbic oxide.}}{\mathbf{Pb}''O} + \mathbf{S}H_2 = \underset{\text{Plumbic sulphide.}}{\mathbf{Pb}''S} + \mathbf{O}H_2.$$

$$\underset{\text{Sodi hydrate.}}{\mathbf{O}NaH} + \mathbf{S}H_2 = \underset{\text{Sodic sulphhydrate.}}{\mathbf{S}''NaH} + \mathbf{O}H_2.$$

$$\underset{\text{Magnesic hydrate.}}{\mathbf{Mg}''Ho_2} + 2\mathbf{S}H_2 = \underset{\text{Magnesic sulphhydrate.}}{\mathbf{Mg}''Hs_2} + 2\mathbf{O}H_2.$$

Since many of the sulphides are scarcely or not at all soluble in water, this gas gives precipitates of sulphides when passed into the solutions of many metallic salts; with a salt of zinc, the precipitate is white; of manganese, flesh-coloured; antimony, orange; arsenic, lemon-yellow; copper, brown-black; lead, black; &c.

Test. A minute trace of sulphuretted hydrogen may be detected by its blackening effect on paper moistened with plumbic acetate.

COMPOUNDS OF THE GROUP WITH CHLORINE, &c.

[Selenious and tellurous chlorides—

$\mathbf{Se}^{iv}Cl_4$ and $\mathbf{Te}^{iv}Cl_4$.]

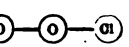
Hypochlorous and hypobromous anhydrides—

$\mathbf{O}Cl_2$ and $\mathbf{O}Br_2$.

[Hyposulphurous (?) and hypotellurous chlorides—

$\mathbf{S}''Cl_2$ and $\mathbf{Te}''Cl_2$.]

Chloric ozide?—

$\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Cl\end{matrix}\right.$ or $'\mathbf{O}'_2Cl_2$ 

[Disulphuric and diselenic dichlorides—

$'\mathbf{S}'_2Cl_2$ and $'\mathbf{Se}'_2Cl_2$.]

Chlorous anhydride—

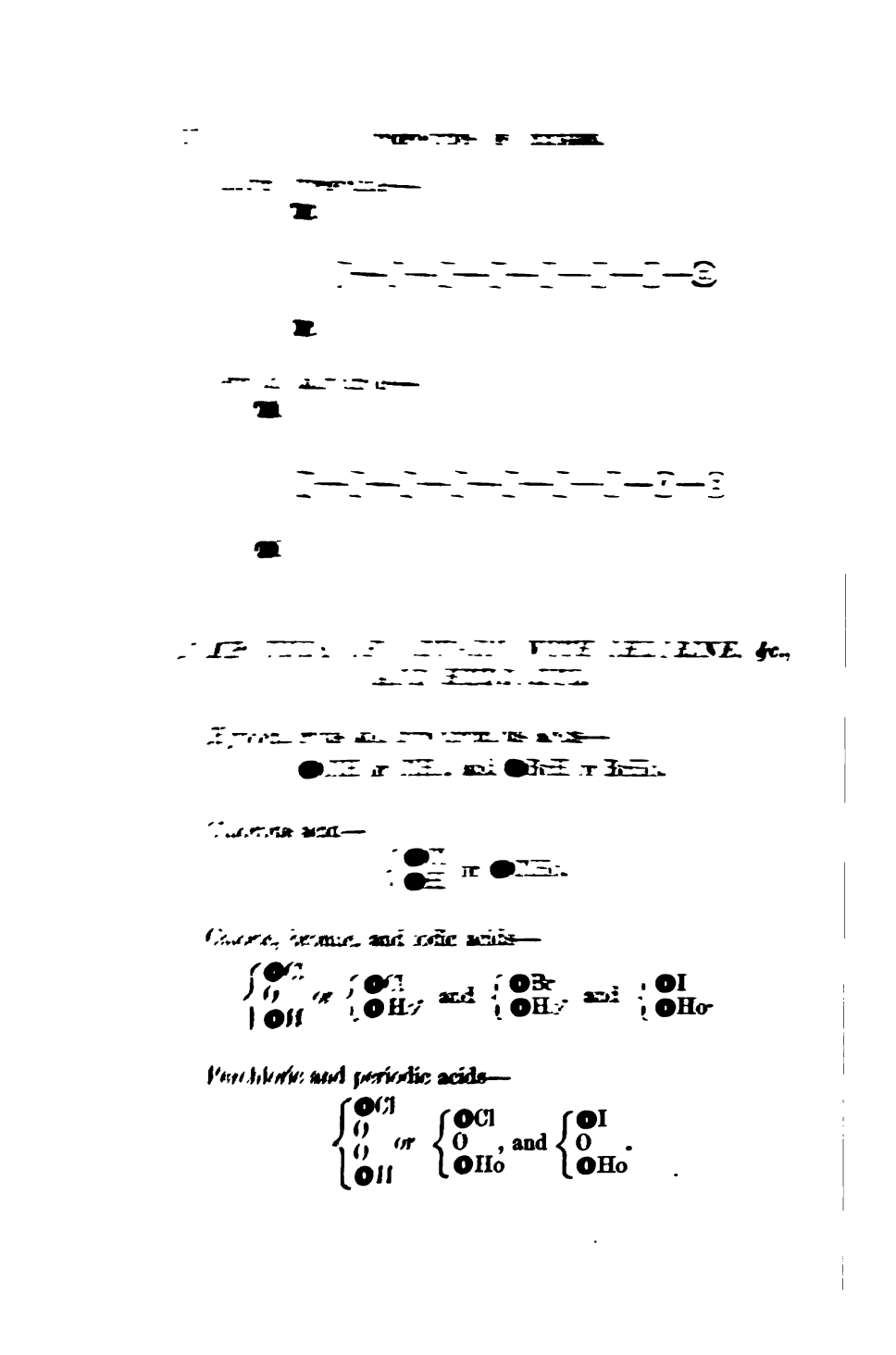
$\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ \mathbf{O}Cl\end{matrix}\right.$

Chloric peroxide—

$\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ O\\ \mathbf{O}Cl\end{matrix}\right.$

Iodic anhydride—

$\left\{\begin{matrix}\mathbf{O}I\\ O\\ O\\ O\\ \mathbf{O}I\end{matrix}\right.$



COMPOUNDS OF SULPHUR, &c., WITH OXYGEN AND HYDROXYL.

Sulphurous, selenious, and tellurous anhydrides—

$\mathbf{S}^{iv}O_2$, $\mathbf{Se}^{iv}O_2$, and $\mathbf{Te}^{iv}O_2$.

Sulphurous, selenious, and tellurous acids—

$\mathbf{S}^{iv}OHo_2$, $\mathbf{Se}^{iv}OHo_2$ (and $\mathbf{Te}^{iv}OHo_2$?).

Sulphuric and telluric anhydrides—

$\mathbf{S}^{vi}O_3$ and $\mathbf{Te}^{vi}O_3$.

Sulphuric, selenic, and telluric acids—

$\mathbf{S}^{vi}O_2Ho_2$, $\mathbf{Se}^{vi}O_2Ho_2$, $\mathbf{Te}^{vi}O_2Ho_2$.

Nordhausen sulphuric acid (*dihydric disulphate*)—

$$\left\{\begin{array}{l}'\mathbf{S}^{v}O_2Ho\\O\\'\mathbf{S}^{v}O_2Ho\end{array}\right.$$

Hyposulphurous acid (*sulphosulphuric acid*)—

$\mathbf{S}^{vi}S''OHo_2$.

Dithionic acid— $'\mathbf{S}^{v}{}_2O_4Ho_2$.

Trithionic acid—

$$\left\{\begin{array}{l}'\mathbf{S}^{v}O_2HO\\S''\\'\mathbf{S}^{v}O_2Ho\end{array}\right.$$

Tetrathionic acid—

$$\left\{\begin{array}{l}'\mathbf{S}^{v}O_2Ho\\S''\\S''\\'\mathbf{S}^{v}O_2Ho\end{array}\right.$$

Pentathionic acid—

$$\left\{\begin{array}{l}'\mathbf{S}^{v}O_2Ho\\S''\\S''\\S''\\'\mathbf{S}^{v}O_2Ho\end{array}\right.$$

SULPHUROUS ANHYDRIDE.

$\mathbf{S^{iv}O_2}$.

Molecular weight = 64. *Molecular vol.* . 1 *litre weighs* 32 *criths. Sp. gr.* 32. *Solid at* — 76°. *Liquid under two atmospheres' pressure at* 7°.

Occurrence. Sulphurous anhydride is evolved from volcanic craters, and is also a common impurity in the atmosphere of towns.

Preparation. 1. Burn sulphur in air or oxygen:

$$S_2 + 2O_2 = 2\mathbf{S^{iv}O_2}.$$

2. Copper clippings or mercury boiled with concentrated sulphuric acid yield this gas. It must be made to bubble through some water in a wash bottle to remove sulphuric acid, and should be collected either over mercury or by downwards displacement:

$$2\underset{\text{Sulphuric acid.}}{\mathbf{S^{vi}O_2Ho_2}} + \text{Cu (or Hg)} = \underset{\text{Cupric or mercuric sulphate.}}{\mathbf{S^{vi}O_2}\text{Cuo}''\text{ (or }\mathbf{S^{vi}O_2}\text{Hgo}'')} + 2\mathbf{O}H_2 + \mathbf{S^{iv}O_2}.$$

3. Charcoal deoxidises sulphuric acid when heated with it; carbonic anhydride also is evolved:

$$2\,\mathbf{S^{vi}O_2Ho_2} + C = 2\mathbf{O}H_2 + 2\mathbf{S^{iv}O_2} + \mathbf{C}O_2.$$

Properties. Sulphurous anhydride, the transparent colourless gas to which the suffocating odour of burning sulphur is due, condenses under the ordinary pressure at — 10°, the temperature of a mixture of ice and salt—or at the normal temperature under a pressure of about two atmospheres—to a transparent, colourless, limpid liquid, which freezes at — 76°,

becoming converted into a colourless, transparent, crystalline solid. The rapid evaporation of liquid sulphurous anhydride may be made to produce so low a temperature as − 60°,—a good illustration of the disappearance of heat, as such, when interior work has to be performed (v. p. 28). Water combines with sulphurous anhydride, of which it dissolves at 0° 68·8 times—and at 15° 43·5 times—its bulk, to form sulphurous acid. The solution resembles the gas in taste and smell; it absorbs oxygen and thus produces sulphuric acid.

Sulphurous anhydride is neither respirable nor inflammable, nor will it support the combustion of a burning match or taper. In the presence of water or moisture, it possesses considerable powers of bleaching. Its mode of combination with water to form sulphurous acid (or hydric sulphite), and with metallic hydrates to form salts called *sulphites*, is represented in the succeeding equations:

$$OH_2 + S^{iv}O_2 = S^{iv}OHo_2.$$
Hydric sulphite.

$$OKH + S^{iv}O_2 = S^{iv}OHoKo.$$
Hydric potassic sulphite.

$$2OKH + S^{iv}O_2 = S^{iv}OKo_2 + OH_2.$$
Normal potassic sulphite.

Uses. In the manufacture of sulphuric acid, sulphurous anhydride plays a very important part. This gas is also used for bleaching and disinfecting purposes.

SULPHUROUS ACID, $S^{iv}OHo_2$.

Molecular weight = 82. *Crystallises at* 0°.

It is difficult to obtain this compound perfectly free from admixture with water. It is a dibasic acid, and converts metallic hydrates into sulphites:

$$\mathbf{O}KH + \mathbf{S}^{iv}OHo_2 = \underset{\text{Hydric potassic sulphite.}}{\mathbf{S}^{iv}OHoKo} + \mathbf{O}H_2.$$

$$2\mathbf{O}KH + \mathbf{S}^{iv}OHo_2 = \underset{\text{Potassic sulphite.}}{\mathbf{S}^{iv}OKo_2} + 2\mathbf{O}H_2.$$

Tests. Sulphites, when treated with strong sulphuric or hydrochloric acid, evolve sulphurous anhydride, to be recognised by its odour.

$$\underset{\text{Potassic sulphite.}}{\mathbf{S}^{iv}OKo_2} + \underset{\text{Sulphuric acid.}}{\mathbf{S}^{vi}O_2Ho_2} = \underset{\text{Potassic sulphate.}}{\mathbf{S}^{vi}O_2Ko_2} + \mathbf{O}H_2 + \mathbf{S}^{iv}O_2.$$

Solutions of sulphites, on the addition of argentic nitrate, give a white precipitate of argentic sulphite :—

$$\underset{\text{Potassic sulphite.}}{\mathbf{S}^{iv}OKo_2} + \underset{\text{Argentic nitrate.}}{2\mathbf{N}^{v}O_2Ago} = \underset{\text{Argentic sulphite.}}{\mathbf{S}^{iv}OAgo_2} + \underset{\text{Potassic nitrate.}}{2\mathbf{N}^{v}O_2Ko}.$$

When boiled with water, this precipitate becomes black, owing to the separation of metallic silver :—

$$\underset{\text{Argentic sulphite.}}{\mathbf{S}^{iv}OAgo_2} + \mathbf{O}H_2 = \underset{\text{Sulphuric acid.}}{\mathbf{S}^{vi}O_2Ho_2} + Ag_2.$$

Uses. The bleaching powers of this acid, or of the anhydride, are applied in many cases where chlorine would be injurious to the substances to be bleached, *e.g.*, straw, wool, isinglass, silk, &c. These are moistened and exposed to the fumes of burning sulphur. Both sulphurous acid and the anhydride are also useful as antiseptics and disinfectants.

SULPHURIC ANHYDRIDE, $\mathbf{S}^{vi}O_3$.

Molec. weight = 80. *Molec vol.* ☐☐. 1 *litre of vapour weighs* 40 *criths. Vap. sp. gr.* 40. *Fusing point*, 24°·5. *Boiling point*, 52°·6.

Preparation. 1. When sulphurous anhydride and oxygen are passed over ignited spongy platinum, they unite:

$$2S^{IV}O_2 + O_2 = 2S^{VI}O_3.$$

2. When Nordhausen sulphuric acid is gently heated in a glass retort, fumes of sulphuric anhydride are produced, which may be condensed in a receiver cooled by ice:—

$$\left\{\begin{matrix}{}'S^{V}O_2Ho \\ 0 \\ {}'S^{V}O_2Ho\end{matrix}\right. = \underset{\text{Sulphuric acid.}}{S^{VI}O_2Ho_2} + S^{VI}O_3.$$

3. On heating disodic disulphate the following decomposition ensues:

$$\left\{\begin{matrix}{}'S^{V}O_2Nao \\ 0 \\ {}'S^{V}O_2Nao\end{matrix}\right. = \underset{\text{Sodic sulphate.}}{S^{VI}O_2Nao_2} + S^{VI}O_3.$$

4. Phosphoric anhydride heated with sulphuric acid becomes converted into phosphoric acid at the expense of the latter:

$$S^{VI}O_2Ho_2 + \underset{\text{Phosphoric anhydride.}}{P^{V}{}_2O_5} = \underset{\text{Meta-phosphoric acid.}}{2P^{V}O_2Ho} + S^{VI}O_3.$$

Properties. This anhydride consists of white fibrous tough ductile needles, with a silky appearance; it fumes in the air, is highly deliquescent, combines with water with the emission of intense heat and a hissing noise, and can only be liberated from the combination by phosphoric anhydride. It does not redden litmus paper, nor does it char dry skin.

SULPHURIC ACID, $S^{VI}O_2Ho_2$.

Molec. weight = 98. *Molecular vol.* (*because of dissociation*). 1 *litre of vapour weighs* 24·5 *criths. Sp. gr.* 1·85. *Boiling point*, 325°.

Manufacture. This acid is perhaps the most important

product, and its preparation the manufacture most extensively carried on, at chemical works. The process employed consists simply in the synthesis of sulphuric acid, from sulphurous anhydride, oxygen, and water :—

$$2S^{iv}O_2 + O_2 + 2OH_2 = 2S^{vi}O_2Ho_2.$$

But the means by which it is usual to obtain the sulphurous anhydride employed, and to supply it with oxygen and water, demand a detailed explanation. Sulphur, which has undergone no other preparation than that of being melted out from its earthy impurities, is burnt on iron plates, in a row of small furnaces; into these a supply of air, much greater than is necessary for the conversion of the sulphur into sulphurous anhydride, is admitted; above the burning sulphur in each furnace hangs an iron pot, containing sodic nitrate and sulphuric acid; the vapours of nitric acid and nitric peroxide evolved from this mixture mingle with the sulphurous anhydride and air, and pass from each furnace through a short, wide, leaden pipe, cooled externally by a reservoir of cold water, into large chambers with leaden walls, supported by massive wooden framework. Water to the depth of a few inches covers the bottom of the chambers; and steam, from a small boiler, is injected into the interior on all sides. It is in these leaden chambers that the synthetic process above described takes place. The nitric acid and oxides of nitrogen obtained from the sodic nitrate supply the oxygen necessary for converting sulphurous anhydride into sulphuric anhydride, whilst the latter, by the simultaneous supply of steam, is converted into sulphuric acid:

$$\underset{\text{Sodic nitrate.}}{2N^{v}O_2Nao} + S^{vi}O_2Ho_2 = \underset{\text{Sodic sulphate.}}{S^{vi}O_2Nao_2} + \underset{\text{Nitric acid.}}{2N^{v}O_2Ho.}$$

$$\underset{\text{Nitric acid.}}{4N^{v}O_2Ho} = 2OH_2 + \underset{\text{Nitric peroxide.}}{2'N^{iv}{}_2O_4} + O_2.$$

$$4S^{iv}O_2 + 2'N^{iv}{}_2O_4 + O_2 + 4OH_2 = 4S^{vi}O_2Ho_2 + 2N'''{}_2O_3.$$

Nitric peroxide. Sulphuric acid. Nitrous anhydride.

The nitrous anhydride which remains is either converted by water into nitric acid (which attacks fresh supplies of sulphurous anhydride) and nitric oxide, or is further reduced by sulphurous anhydride, with the formation of nitric oxide (and probably also of some nitrous oxide).

$$3N'''{}_2O_3 + OH_2 = 2N^{v}O_2Ho + 2'N''{}_2O_2.$$

Nitrous anhydride. Nitric acid. Nitric oxide.

$$N'''{}_2O_3 + S^{iv}O_2 + OH_2 = S^{vi}O_2Ho_2 + 'N''{}_2O_2$$

Nitrous anhydride. Sulphuric acid. Nitric oxide.

Nitric oxide, in contact with the excess of air admitted through the furnaces, reproduces nitric peroxide, which also in turn oxidises more sulphurous anhydride:

$$'N''{}_2O_2 + O_2 = 'N^{iv}{}_2O_4.$$

Thus the products of the sodic nitrate are able to act continuously again and again, as carriers of oxygen from the air to the sulphurous anhydride; and it would be unnecessary to supply fresh quantities of these carriers, were it not that a portion is continually escaping into the tall chimney with which the chambers are connected, whilst some nitrous anhydride is wasted by reduction to nitrous oxide. Between the chimney and the leaden chambers the gases leaving the latter are made to pass through some leaden towers filled with coke, which arrests any sulphuric acid which may have eluded absorption by the water covering the floor of the chambers. Strong sulphuric acid is liable to absorb nitric oxide; the acid drawn off from the chambers should therefore have a specific gravity under 1·6; it is next concentrated to a density of about 1·7 in leaden pans or tanks, placed in iron plates over hot fires. The acid thus produced is the *brown oil of vitriol* of commerce,

and may either be sold in this form, or may be concentrated still further in a platinum or glass retort, from the bottom of which the strong acid, which would attack lead, and has a specific gravity of 1·84 to 1·85, and the composition $\mathbf{S^{vi}}O_2Ho_2$, is drawn off by means of a siphon, whilst the water and acid which distil over are returned to the chambers or the evaporating pans.

The only impurity of much consequence in sulphuric acid thus prepared is a small quantity of plumbic sulphate; this is detected on dilution, when it is precipitated as a white powder. All traces of lead may be removed by subjecting the acid to distillation. Iron pyrites are frequently substituted for sulphur, as the source of sulphurous anhydride, with this serious disadvantage, that they almost invariably contain and contaminate the acid with arsenic, a very troublesome impurity, detected by several tests, of which the yellow precipitate formed in the dilute acid by sulphuretted hydrogen is one.

Sulphuric acid may also be prepared in the laboratory by three other methods:—

1. The addition of water to sulphuric anhydride:

$$\mathbf{S^{vi}}O_3 + \mathbf{O}H_2 = \mathbf{S^{vi}}O_2Ho_2.$$

2. The combination of sulphurous anhydride and hydroxyl:

$$\mathbf{S^{iv}}O_2 + Ho_2 = \mathbf{S^{vi}}O_2Ho_2.$$

3. The exposure of sulphurous acid to the action of the air:

$$2\mathbf{S^{iv}}OHo_2 + O_2 = 2\mathbf{S^{vi}}O_2Ho_2.$$

Properties. Sulphuric acid, hydric sulphate, or "oil of vitriol" thus manufactured is a brownish, oily liquid, which boils at about 325°, and freezes at a low temperature, melting again at about 10°·5.

It combines violently—almost explosively unless precautions are observed—with water, with the extrication of much heat; it absorbs moisture rapidly from the air, and should

hence be kept in bottles with tight-fitting stoppers; in the laboratory it is a valuable desiccating agent. Sulphuric acid chars such organic bodies as wood, straw, sugar, &c., whilst from others, such as alcohol, &c., it abstracts the elements of water, converting them into fresh compounds.

This acid is dibasic, and resembles sulphurous acid in forming two principal classes of salts with monad metals, exemplified by hydric potassic sulphate—$\mathbf{S}^{vi}O_2HoKo$—and normal potassic sulphate—$\mathbf{S}^{vi}O_2Ko_2$. Concentrated sulphuric acid has but a feeble action on metals in the cold; but, when it is boiled with such metals as copper, mercury, arsenic, tin, lead, silver, &c., sulphurous anhydride and the sulphate of the metal are simultaneously formed, *e.g.*:—

$$2\mathbf{S}^{vi}O_2Ho_2 + Ag_2 = \mathbf{S}^{vi}O_2Ago_2 + 2\mathbf{O}H_2 + \mathbf{S}^{iv}O_2.$$

Gold, platinum, and similar metals undergo no change even when boiled with sulphuric acid. Some other metals, such as zinc and iron, are dissolved by this acid in the cold with evolution of hydrogen—as in the process for the preparation of that gas. A compound of sulphuric acid with a molecule of water is formed when water is added to sulphuric acid till the mixture has a density of 1·78. This compound may be frozen in rhombic prisms, and is hence sometimes called *glacial sulphuric acid.*

Uses. The *brown* acid of commerce is used for the manufacture of the so-called "superphosphate of lime" for manure, &c. The manufacture of sodic sulphate (as a step in the production of sodic carbonate), and of hydrochloric and nitric acids and other important compounds, consumes large quantities of sulphuric acid. It is perhaps the most important reagent in the laboratory.

Test. Sulphuric acid or the aqueous solution of a sulphate gives, with baric nitrate, a white precipitate of baric sulphate, very insoluble in nitric acid (See p. 51 n.):—

$\mathbf{S}^{vi}O_2Ho_2$	+	$\mathbf{N}^{v}{}_2O_4Bao''$	=	$\mathbf{S}^{vi}O_2Bao''$	+	$2\mathbf{N}^{v}O_2Ho.$
Sulphuric acid.		Baric nitrate.		Baric sulphate.		Nitric acid.

Chapter XVI.

ARTIADS. SECTION 2.

CARBON, SILICON, TITANIUM, and TIN.

Since these elements—the basylous artiads—are all tetrequivalent, their compounds present considerable analogies. There is a close resemblance between some of the properties of silicon and carbon, and also between those of the metals titanium and tin.

SILICON, Si.

Atomic Weight = 28·5. *Sp. gr. (graphitoid form)* = 2·49. *Equivalence* iv.

Occurrence. Silicon, although after oxygen perhaps the most abundant of the elements, exists only in the combined state,—either with oxygen as flint (Lat. *silex*, whence the name), sand, quartz, rock-crystal, opal, chalcedony, &c., or with metals and oxygen in metallic silicates.

Silicon is obtained in as many as three allotropic forms corresponding to the three forms of carbon.

i. Amorphous Silicon.—*Preparation.* Heat with concentrated sulphuric acid some ground flints mixed with fluor-spar (calcic fluoride). Dissolve the gaseous silicic fluoride produced in water, and neutralise the acid solution with potash. The following reactions take place, and an almost insoluble salt—potassic silicofluoride—is obtained:—

$$\underset{\text{Silicic anhydride.}}{\mathbf{Si^{iv}}O_2} + \underset{\text{Calcic fluoride.}}{2\mathbf{Ca}''F_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S^{vi}}O_2Ho_2} = \underset{\text{Silicic fluoride.}}{\mathbf{Si^{iv}}F_4} + \underset{\text{Dihydric calcic sulphate.}}{2\mathbf{S^{vi}}OHo_2Cao''}.$$

$$3\mathbf{Si^{IV}}F_4 + 4\mathbf{O}H_2 = \mathbf{Si^{IV}}Ho_4 + 2(\mathbf{Si^{IV}}F_4,2HF).$$
Silicic fluoride. Silicic acid. Hydrofluosilicic acid.

$$\mathbf{Si^{IV}}F_4,2HF + 2\mathbf{O}KH = \mathbf{Si^{IV}}F_4,2KF + 2\mathbf{O}H_2.$$
Hydrofluosilicic acid. Potassic silicofluoride.

This salt, when dry, is mixed with eight or nine-tenths of its weight of potassium in a glass or iron tube and heated, after which the excess of potassium is removed by careful washing :—

$$\mathbf{Si^{IV}}F_4,2KF + 2K_2 = Si + 6KF.$$
Potassic silicofluoride. Potassic fluoride.

Properties. Silicon thus obtained is a brown, amorphous powder, insoluble in water, nitric acid, or sulphuric acid, but soluble in hydrofluoric acid :—

$$Si + 6HF = \mathbf{Si^{IV}}F_4,2HF + 2H_2.$$

Potassic silicate is formed when amorphous silicon is fused or boiled with potash :—

$$Si + 4\mathbf{O}KH = \mathbf{Si^{IV}}Ko_4 + 2H_2.$$

When amorphous silicon is heated in air or oxygen it burns brilliantly, and becomes coated with fused silicic anhydride, which protects it from further oxidation.

ii. Graphitoid Silicon is prepared by heating amorphous silicon intensely, as well as by other processes.

Properties. The dense, black, lustrous, hexagonal plates obtained may be heated to whiteness in oxygen without change, may be dissolved by mixed nitric and hydrofluoric acids, though not by pure hydrofluoric acid, and oxidise very slowly when heated with fused potash.

iii. Crystalline or Adamantine Silicon separates when aluminium is powerfully heated in a current of the vapour of silicic chloride. The aluminic chloride produced volatilises :—

$$3\mathbf{Si^{IV}}Cl_4 + 2Al_2 = 2'\mathbf{Al'''}_2Cl_6 + Si_3.$$

Properties. The crystals are hard enough to cut glass, and have a fusing-point, according to Deville, between that of cast iron and that of steel.

TITANIUM AND TIN will be more conveniently studied with the other metals than at this place. The analogies of their compounds—which, with the exception of the stannous and titanous and distannic and dititanic compounds, are on the marsh-gas ($\mathbf{C}H_4$) type—with oxides those of carbon and silicon, will be perceived by a glance at the succeeding lists.

COMPOUNDS OF THE GROUP WITH HYDROGEN.

Ethylene ..... $\mathbf{C}''_2H_4$.
Marsh-gas..... $\mathbf{C}^{IV}H_4$.
Silicic hydride (a spontaneously inflammable gas, never obtained free from hydrogen) ..... $\mathbf{Si}^{IV}H_4$.

Tin and titanium do not, so far as we know, combine with hydrogen.

COMPOUNDS OF THE GROUP WITH CHLORINE, &c.

Stannous chloride—$\mathbf{Sn}''Cl_2$.

Dicarbonic and dititanic hexachlorides—

$$\left\{\begin{matrix}\mathbf{C}Cl_3\\ \mathbf{C}Cl_3\end{matrix}\right. \text{ and } \left\{\begin{matrix}\mathbf{Ti}Cl_3\\ \mathbf{Ti}Cl_3\end{matrix}\right.$$

Carbonic, titanic, and stannic tetrachlorides—

$\mathbf{C}Cl_4$, $\mathbf{Ti}Cl_4$, and $\mathbf{Sn}Cl_4$.

Silicic chloride, bromide, and fluoride—

$\mathbf{Si}Cl_4$, $\mathbf{Si}Br_4$, and $\mathbf{Si}F_4$.

COMPOUNDS OF THE GROUP WITH OXYGEN, &c., AND HYDROXYL.

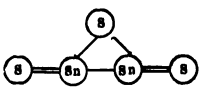
Carbonic, titanous, and stannous oxides—

C″O, **Sn**″O, and **Ti**″O.

Stannous sulphide—**Sn**″S″.

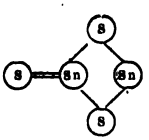
Distannic trioxide and trisulphide—

$\left\{ \begin{matrix} {}'\mathbf{Sn}'''\mathrm{O} \\ {}'\mathbf{Sn}'''\mathrm{O} \end{matrix} \right\}$O, and $\left\{ \begin{matrix} {}'\mathbf{Sn}'''\mathrm{S}'' \\ {}'\mathbf{Sn}'''\mathrm{S}'' \end{matrix} \right\}$S″,



or stannous stannate and sulphostannate—

Sn^{iv}OSno″ and **Sn**^{iv}S″Sns″.



Carbonic, silicic, titanic, and stannic anhydrides—

$\mathbf{C}O_2$, $\mathbf{Si}^{iv}O_2$, $\mathbf{Ti}^{iv}O_2$, and $\mathbf{Sn}^{iv}O_2$.

Carbonic,* silicic (dibasic), titanic, and stannic acids—

$\mathbf{C}OHo_2$, $\mathbf{Si}^{iv}OHo_2$, $\mathbf{Ti}^{iv}OHo_2$, and $\mathbf{Sn}^{iv}OHo_2$.

Silicic acid (tetrabasic)—$\mathbf{Si}^{iv}Ho_4$.

Carbonic, silicic, titanic, and stannic sulphides—

$\mathbf{C}S_2$, $\mathbf{Si}^{iv}S_2$, $\mathbf{Ti}^{iv}S_2$, and $\mathbf{Sn}^{iv}S_2$.

Sulphocarbonic acid—$\mathbf{C}S''Hs_2$.

* Not isolated hitherto.

CARBONIC ANHYDRIDE, CO_2.

Molecular weight = 44. *Molecular volume* □□. 1 *litre weighs* 22 *criths. Sp. gr.* 22. *Fusing point* — 57°. *Boils below its fusing-point* (*at* — 78°).

Occurrence. This gas—generally known by the name "carbonic acid," now restricted to its compound with water—we have already noticed as a most important component of atmospheric air, though on the average it constitutes but $\frac{1}{1100}$th part of the bulk of the atmosphere. Its presence is readily demonstrated by leaving some lime-water in a saucer exposed to the air; in a few minutes a white scum forms on the surface of the liquid and sinks when agitated to the bottom. This consists of chalk or calcic carbonate and is due to the combination of the lime with free carbonic anhydride. This gas is a product of respiration, putrefaction, fermentation, and decay, and is evolved during the formation of coal, as "choke-damp," and from volcanic craters, and also from lime-kilns.

Preparation. 1. Any form of carbon yields carbonic anhydride when burnt in excess of air or oxygen:

$$C + O_2 = CO_2.$$

2. *The Best Method.* Decompose a carbonate by means of a strong acid; hydrochloric acid and marble, or some other form of calcic carbonate, are usually employed;

$$\underset{\text{Calcic carbonate.}}{COCao''} + 2HCl = \underset{\text{Calcic chloride.}}{Ca''Cl_2} + OH_2 + CO_2.$$

Properties. The transparent and colourless gas evolved has a faintly acid taste and smell. When generated in strong closed vessels it is condensed to a colourless, transparent, and very mobile liquid, which requires a pressure of 38·5 atmospheres at 0°, or of 60 atmospheres at 15°, to keep it in the

liquid state, and which expands more rapidly when heated than the gaseous anhydride. When a jet of the liquid is thrown into the air, part returns suddenly to the gaseous state, abstracting such a quantity of heat that the remainder is solidified as a snow-like substance. This solid—on account of the low conductivity for heat of the gas which it is continually producing—does not blister the fingers unless pressed between them; it is employed in the production of very low temperatures; mixed with ether and placed in the vacuum of the air-pump, it produces a temperature (— 100°) considerably below that at which mercury freezes; mercury may even be frozen in a red-hot platinum crucible by means of lumps of carbonic anhydride and a little ether; when mercury thus solidified is placed in water it fuses, and every stream of melting metal becomes inclosed in an icicle. Liquid carbonic anhydride does not mix freely with water but is soluble in alcohol, ether, &c. Carbonic anhydride gas is more than half as heavy again as air, and may be poured from one vessel into another without much loss or admixture. A soap-bubble of atmospheric air will float on the surface of a jar of carbonic anhydride. At the ordinary temperature water absorbs about its own volume of carbonic anhydride, at 0° about 1·797 times its volume. At a fixed temperature water dissolves the same bulk of the gas whatever may be the pressure; for example, if the pressure be doubled, and the density of the gas consequently also doubled (v. p. 116), so long as the temperature remains constant, twice the weight of carbonic anhydride, but yet the same volume, is absorbed. When the pressure is again reduced the gas escapes with effervescence, as when a bottle of *soda-water* is opened.

Pure carbonic anhydride produces spasm of the glottis, and is consequently irrespirable; mixed with less than 99·6 or 99·7 per cent. of air it is a narcotic poison; and, since even 0·2 per cent. of this gas is a proportion rendering air unfit for continued respiration, the thorough ventilation of crowded rooms, public buildings, and coal-mines, is a matter of the first

importance. Even when mixed with much air, carbonic anhydride extinguishes every form of combustion. It is quite incombustible. When passed over iron or carbon heated to redness it loses half its oxygen. Carbonic oxide is similarly separated when carbonic anhydride is decomposed by the electric spark. Heated potassium has the following action:

$$3\mathbf{C}O_2 + 2K_2 = \underset{\text{Potassic carbonate.}}{2\mathbf{C}OKo_2} + C.$$

A solution of carbonic anhydride reddens litmus, producing a colour less pronounced than that given by stronger acids, and also less permanent, since boiling liberates the carbonic anhydride and restores the blue colour. In nature carbonic acid is a great solvent and disintegrator of rocks. With metallic oxides and hydrates carbonic anhydride produces carbonates:

$$\underset{\text{Baric oxide.}}{\mathbf{Ba}''O} + \mathbf{C}O_2 = \underset{\text{Baric carbonate.}}{\mathbf{C}OBao''}.$$

$$KHo + \mathbf{C}O_2 = \underset{\text{Hydric potassic carbonate.}}{\mathbf{C}OHoKo}.$$

$$2KHo + \mathbf{C}O_2 = \underset{\text{Potassic carbonate.}}{\mathbf{C}OKo_2} + \mathbf{O}H_2.$$

$$\underset{\text{Calcic hydrate.}}{\mathbf{Ca}''Ho_2} + \mathbf{C}O_2 = \underset{\text{Calcic carbonate.}}{\mathbf{C}OCao''} + \mathbf{O}H_2.$$

The two classes of salts formed by carbonic acid, a dibasic acid, are exemplified by hydric potassic carbonate and potassic carbonate. Carbonic acid—$\mathbf{C}OHo_2$—has never been isolated.

Test. Carbonic anhydride is evolved from any carbonate treated with strong acid, and gives a white precipitate of chalk when passed into lime-water, or of baric carbonate when agitated with baryta-water. Excess of the gas redissolves the precipitates.

Uses. Carbonic anhydride is essential to the respiration of plants. Some successful efforts have been made to apply this gas to the extinction of fires in coal-mines.

CARBONIC OXIDE, C″O.

Molec. weight = 28. *Molec vol.* □□. 1 *litre weighs* 14 *criths. Sp. gr.* 14.

Preparation. 1. Pass carbonic anhydride over red-hot charcoal, or burn carbon or a fuel in a limited supply of air :—

$$CO_2 + C = 2C''O.$$

In an open fire the flickering blue flame of carbonic oxide may often be seen. In this case its presence is due to the formation of carbonic anhydride at the bottom of the grate where there is a plentiful supply of air, and to the subsequent reduction of this higher oxide of carbon during its passage over red-hot coal or coke.

2. Pass carbonic anhydride over red-hot iron :—

$$4CO_2 + Fe_3 = \begin{cases} 'Fe'''O \\ ''Fe''O \\ 'Fe'''O \end{cases} + 4C''O.$$

Triferric tetroxide.*

3. Heat iron, zinc, or carbon with a carbonate :—

$$COCao'' + C = Ca''O + 2C''O.$$

Calcic carbonate. Calcic oxide.

4. Treat oxalic acid with some substance that has a powerful attraction for water, such as sulphuric acid, and—in order to separate the carbonic anhydride simultaneously formed—pass the gases through sodic hydrate :—

* See the graphic formula for Mn_3O_4 on p. 77.

$$\left.\begin{matrix}\mathbf{C}\text{OHo}\\ \mathbf{C}\text{OHo}\end{matrix}\right\} = \mathbf{O}H_2 + \mathbf{C}O_2 + \mathbf{C}''O.$$

Oxalic acid.

5. Heat potassic ferrocyanide with sulphuric acid:—

$$\mathbf{Fe}''(\mathbf{CN}''')_2, 4\mathbf{KCN} + 6\mathbf{S}^{vi}O_2Ho_2 + 7\mathbf{O}H_2 =$$

Potassic ferrocyanide.

$$2\mathbf{S}^{vi}O_2Ko_2 + 3\mathbf{S}^{vi}O_2(NH_4O)_2 + \mathbf{S}^{vi}OHo_2Feo'' + 6\mathbf{C}''O.$$

Potassic sulphate. Ammonic sulphate. Ferrous sulphate.

Properties. Carbonic oxide is a transparent, colourless, tasteless, inodorous gas, almost as heavy as air. It has never been liquefied, and is scarcely soluble in water.

This gas is poisonous even when mixed with much air, and, since it is produced in open charcoal stoves, has been a frequent cause of deaths. It burns with a blue flame, becoming converted into carbonic anhydride, and does not support combustion. It is absorbed by a solution of cuprous chloride—$'\mathbf{Cu}'_2Cl_2$—in hydrochloric acid, and at a high temperature by potassic hydrate and by potassium.

Use. The flame of carbonic oxide is an important reducing agent in some metallurgical operations.

SILICIC ANHYDRIDE SILICA $\mathbf{Si}^{iv}O_2$.

Molec. weight = 60·5. *Sp. gr.* 2·69.

Occurrence. As we have already observed, silica is abundant as sand, quartz, &c., and silicon is not found in nature otherwise than in the form of silica and the silicates.

Preparation. Silica assumes two forms: in the *crystalline* form it occurs quite free from impurity in *rock crystal* and some kinds of quartz, &c. The *amorphous* variety may be obtained by heating to 100° the silicic acid (tetrabasic $\mathbf{Si}^{iv}Ho_4$, dibasic $\mathbf{Si}^{iv}OHo_2$) prepared by any of the following processes:—

1. To a mixture of sodic and potassic carbonates fused by

a red-heat add one-third of its weight of finely powdered crystalline silica (ground flint, for example) in small quantities. When the carbonic anhydride has escaped with effervescence, heat strongly; afterwards cool the mass, dissolve it slowly in water, treat the solution of sodic and potassic silicates with hydrochloric acid, and evaporate. A gelatinous hydrate of silica is thus obtained :—

$$\underset{\text{Sodic silicate.}}{\mathbf{Si^{iv}}Nao_4} + \underset{\text{Potassic silicate.}}{\mathbf{Si^{iv}}Ko_4} + 8HCl = \underset{\text{Sodic chloride.}}{4NaCl} + \underset{\text{Potassic chloride.}}{4KCl} + \underset{\text{Silicic acid.}}{2\mathbf{Si^{iv}}Ho_4}.$$

2. Pass carbonic anhydride into a solution of a soluble silicate :—

$$\underset{\text{Sodic silicate.}}{\mathbf{Si^{iv}}Nao_4} + 4\mathbf{O}H_2 + 4\mathbf{C}O_2 = \underset{\text{Hydric sodic carbonate.}}{4\mathbf{C}OHoNao} + \mathbf{Si^{iv}}Ho_4.$$

Granitic and other hard rocks are disintegrated by this action of dissolved carbonic anhydride on silicates.

3. Pure silica results from the transmission of gaseous silicic fluoride (obtained by heating silicic anhydride with calcic fluoride and sulphuric acid) through water :—

$$\mathbf{Si^{iv}}O_2 + \underset{\text{Calcic fluoride.}}{2\mathbf{Ca}''F_2} + 2\mathbf{S^{vi}}O_2Ho_2 = \underset{\text{Dihydric calcic sulphate.}}{2\mathbf{S^{vi}}OHo_2Cao''} + \underset{\text{Silicic fluoride.}}{\mathbf{Si^{iv}}F_4}.$$

$$3\mathbf{Si^{iv}}F_4 + 4\mathbf{O}H_2 = \underset{\text{Hydrofluosilicic acid.}}{2\mathbf{Si^{iv}}F_4, 2HF} + \mathbf{Si^{iv}}Ho_4.$$

Properties. Pure crystalline silica is transparent, colourless, and tasteless, and hard enough to scratch glass. It occurs in six-sided prisms, terminated by six-sided pyramids. It needs for its fusion the heat of the oxy-hydrogen blowpipe, and melts to a transparent glass, which may be drawn

out into elastic threads of the amorphous variety. Though ordinarily not volatile, silicic anhydride is said to be capable of partial sublimation in a current of steam. It is insoluble in water and alkaline solutions, and in all acids except hydrofluoric acid. Amorphous silica obtained as a fine white powder is much more readily dissolved.

Though the gradual addition of hydrochloric acid to the solution of an alkaline silicate precipitates, as we have seen, a gelatinous hydrate of silica, the silica may be held in solution by reversing the experiment and pouring into an excess of hydrochloric acid a dilute solution of an alkaline silicate. By boiling the liquid in a flask the percentage of silica dissolved may be increased to five per cent. Mr. Graham has discovered that a pure aqueous solution of silicic acid may be separated by letting this solution in hydrochloric acid *dialyse* or diffuse through a membrane. The tasteless and colourless solution obtained has a somewhat stronger acid reaction than carbonic acid. It coagulates when kept. Several hydrates of silica have been prepared.

The silicates are an abundant and important class of minerals. The following are the chemical names and formulæ of a few selected as examples:—

Talc, *tetramagnesic pentasilicate* .... $Si^{iv}_5O_6Mgo''_4$.

Serpentine, *dihydric trimagnesic disilicate* ..... $\begin{cases} SiHoMgo'' \\ Mgo'' \\ SiHoMgo''. \end{cases}$

Meerschaum, *tetrahydric dimagnesic trisilicate* ..... $\begin{cases} SiHoMgo'' \\ O \\ SiHo_2 \\ O \\ SiHoMgo''. \end{cases}$

Emerald, *triglucinic aluminic hexasilicate* ..... $Si^{iv}_6O_6('Al'''_2O_6)^{vi}Glo''_3$.

Felspar. Orthose, *dipotassic aluminic hexasilicate* ..... $Si^{iv}_6O_8Ko_2('Al'''_2O_6)^{vi}$.

Chapter XVII.

TRIADS AND PENTADS—SECTION I.

BORON, B_2.

Atomic weight = 11. *Probable molec. weight* = 22. *Equivalence* iii.

Occurrence. Boron is found only in combination and is not an abundant element. Borax—an abnormal sodic borate, $\mathbf{B}'''_4O_5Na_2,10\mathbf{O}H_2$—occurs in the mineral *tincal*. The jets of steam (*fumerolles* or *soffioni*) which issue from the earth in Tuscany contain boric acid. Amongst the resemblances to silicon and carbon which—in spite of its different equivalence—boron evinces, is its appearance under three distinct shapes: the amorphous, the graphitoid, and the crystalline.

i. Amorphous boron is separated when boric anhydride, obtained by fusing boric acid at a red-heat, is heated with sodium:

$$\underset{\text{Boric anhydride.}}{\mathbf{B}'''_2O_3} + 3Na_2 = \underset{\text{Sodic oxide.}}{3\mathbf{O}Na_2} + B_2.$$

Properties. Amorphous boron is a brownish or olive-green powder, slightly soluble in water. It is not oxidised by cold air, water or alkalies, but only by nitric acid or *aqua regia* (a mixture of nitric and hydrochloric acids), and when deflagrated with nitre or ignited with potash. Heated in air or oxygen it takes fire below a red-heat, burns with a reddish light, and scintillates, but soon becomes protected from further combustion by a covering of fused boric anhydride. Amorphous boron may be made to unite directly with nitrogen:

$$B_2 + N_2 = \underset{\text{Boric nitride.}}{2\mathbf{B}'''N}.$$

ii. GRAPHITOID BORON, in pale, copper-coloured, opaque, six-sided plates, is formed when boric chloride is passed over fused aluminium:

$$Al_3 + 2\mathbf{B}'''Cl_3 = {}'\mathbf{Al}'''_2Cl_6 + B_2.$$

Boric chloride. Aluminic chloride.

and also, along with diamond boron, in the following process:—

iii. DIAMOND OR CRYSTALLINE BORON. This, with some graphitoid boron, is produced when amorphous boron is fused with aluminium; also when aluminium and boric anhydride are fused together:

$$\mathbf{B}'''_2O_3 + Al_2 = {}'\mathbf{Al}'''_2O_3 + B_2.$$

Boric anhydride. Aluminic oxide.

Properties. The crystals are generally transparent but brown prisms with a square base, are nearly as hard and refract light almost as powerfully as diamonds, will scratch the ruby, have the specific gravity 2·68, have never been melted, and are insoluble in acids. Crystalline boron burns in oxygen when heated to whiteness, but becomes coated with boric anhydride. All forms of boron burn freely in chlorine. No compound of boron with hydrogen is known.

COMPOUNDS OF BORON WITH CHLORINE, &c.

Boric chloride.....	$\mathbf{B}'''Cl_3$.
Boric bromide and fluoride....	$\mathbf{B}'''Br_3$ and $\mathbf{B}'''F_3$.

COMPOUNDS WITH OXYGEN, &c., AND HYDROXYL.

Boric anhydride	$\mathbf{B}'''_2O_3$.
Monobasic boric acid.....	$\mathbf{B}'''OHo$.
Tribasic boric acid.....	$\mathbf{B}'''Ho_3$.
Boric sulphide.....	$\mathbf{B}'''_2S_3$.

TRIADS AND PENTADS—SECTION 2.

NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, and BISMUTH.

This section comprises all the pentads with which we are acquainted. The *active equivalence* of each member of the group frequently becomes reduced to that of a triad, whilst nitrogen in a few cases is apparently but a monad, its *latent equivalence* being increased from ii to iv (see p. 62).

The remarkable correspondence in structure that exists between the compounds of these five elements justifies their association in one group, although arsenic, antimony, and bismuth belong to the class of elements called metals. Their more simple and important compounds will be found to be built up on the following *types* (see p. 141):—

$$\mathbf{N}'''H_3,\ \mathbf{N}^{v}H_4Cl,\ \mathbf{N}'''_2O_3,\ \mathbf{N}^{v}_2O_5.$$

PHOSPHORUS, P_4.

Atomic weight = 31. *Molec. weight* = 124. *Molec. vol.* □□. 1 *litre of vapour weighs* 62 *criths. Sp. gr.* 1·83. *Vap. sp. gr.* 62. *Fuses at* 44°—45°. *Boils at* 290°. *Equivalence* iii and v.

Occurrence. Phosphorus, combined with oxygen and calcium and other metals, is present in the most ancient formations, and consequently in the greater part of the earth's rocks and soils. Hence it passes into plants and is supplied by them to animals, forming an essential constituent of their nervous systems and brains, and also of their bones, urine, and excrements. This element was discovered by Brande in 1669, and first investigated by Scheele a century later.

Preparation. When calcined bones are digested for 24 hours with concentrated sulphuric acid, the tricalcic diphosphate, of which the bone-ash chiefly consists, is converted into tetrahydric calcic phosphate (the valuable manure commonly called *superphosphate of lime*) which—after extraction by water from the calcic sulphate, filtration, and evaporation to the consistence of a syrup—is mixed with powdered charcoal, and constantly stirred whilst it is evaporated to dryness. The mixture is finally distilled in an earthern retort at a heat slowly raised to redness, and the phosphorous vapours evolved are delivered under water by means of a wide copper or earthen tube:—

$$\underset{\text{Tricalcic diphosphate.}}{P^{v}_{2}O_{2}Cao''_{3}} + 2\underset{\text{Calcic sulphate.}}{S^{vi}O_{2}Ho_{2}} = 2S^{vi}O_{2}Cao'' + \underset{\text{Tetrahydric calcic diphosphate.}}{P^{v}_{2}O_{2}Ho_{4}Cao''}.$$

$$\underset{\text{Tetrahydric calcic diphosphate.}}{P^{v}_{2}O_{2}Ho_{4}Cao''} = \underset{\text{Calcic metaphosphate.}}{P^{v}_{2}O_{4}Cao''} + OH_{2}.$$

$$3\underset{\text{Calcic metaphosphate.}}{P^{v}_{2}O_{4}Cao''} + C_{10} = \underset{\text{Tricalcic diphosphate.}}{P^{v}_{2}O_{2}Cao''_{3}} + 10\underset{\text{Carbonic oxide.}}{CO} + P_{4}.$$

The yellow drops of phosphorus thus condensed may be purified by being fused below warm water, pressed through wash-leather, and finally cast into sticks which must be preserved under cold water.

Properties. The almost transparent, slightly yellowish, wax-like substance obtained by the foregoing process, is only one of several forms in which this element may be procured; it emits in the air white fumes and an odour of garlic. It is soft, except at low temperatures, which render it hard and brittle. Whether solid or melted, phosphorus is a non-conductor of electricity. At about 44° it melts and forms a transparent fluid which boils at 290°, producing colourless vapour. This form of phosphorus is insoluble in water, but soluble in phosphorous trichloride and carbonic disulphide, and

slightly soluble in ether; if its solution in carbonic disulphide is allowed to drop on filter-paper, the solvent evaporates, and the finely-divided phosphorus bursts into flame spontaneously. When this solution is evaporated slowly in a current of hydrogen or carbonic anhydride, the phosphorus crystallises in rhombic dodecahedra.

The vitreous variety of phosphorus, the physical properties of which we have noticed, is exceedingly inflammable, and takes fire in the open air, at a temperature but little higher than its fusing-point, producing phosphoric anhydride. Its igniting-point is still lower when all impurities have not been removed; and, since a blow, or gentle friction, or even the warmth of the hand is sufficient to cause phosphorus to inflame, very great care should be taken in handling it; whilst in cutting it the precaution of keeping it under water should be observed. The burns which phosphorus produces are frequently most serious. At all temperatures above zero, phosphorus undergoes slow combustion in the air, giving off white fumes of phosphorous anhydride, and producing a pale *phosphorescent* light in the dark, hence the name phosphorus, (φῶς, light, φέρω, I bear). This form of phosphorus is highly poisonous.

White or *opaque* phosphorus is formed when sticks of ordinary phosphorus are kept under water and exposed to light. *Black* and *opaque* phosphorus results from the sudden cooling of melted phosphorus. A *viscous* modification has been obtained from very pure phosphorus, heated nearly to its boiling-point, and suddenly cooled.

Red or *amorphous* phosphorus, one of the most interesting instances of allotropy with which we are acquainted, is prepared by maintaining vitreous phosphorus steadily for several hours at a heat of from 230°—250° in closed vessels, in some gas, such as carbonic anhydride, which is incapable of combination with it. The red, opaque powder obtained may be completely freed from remnants of ordinary phosphorus, by digestion with carbonic disulphide, in which it is not soluble.

According to Sir B. Brodie its specific gravity is 2·14. At about 260° it melts, re-assuming the properties of ordinary vitreous phosphorus, and bursts into flame; below this temperature it may be preserved in air for any length of time without oxidation. Amorphous phosphorus is not poisonous.

Uses. The manufacture of lucifer matches, in which phosphorus is largely employed, is attended with great danger—both from the risk of explosion, and from the serious disease of the lower jaw to which the operatives exposed to the fumes of phosphorus are liable—unless the red variety be substituted for vitreous phosphorus. The safety-matches which are coming into use have, in addition to these advantages of amorphous over ordinary phosphorus, this important recommendation, that they are incapable of ignition by friction on any surface except that provided on the box, since the amorphous phosphorus is mixed with the grit of the rubbing surface, and not with the ingredients of the match.

ARSENIC, As, ANTIMONY, Sb, and BISMUTH, Bi.

The study of these elements may be postponed with advantage, until the whole of the metals come under review.

COMPOUNDS OF THE GROUP WITH HYDROGEN.

We are not acquainted with any compound of bismuth with hydrogen; the other members of the group form the following compounds:—

Ammonia	$\mathbf{N}'''H_3$.
Gaseous phosphoretted hydrogen ..	$\mathbf{P}'''H_3$.
Arseniuretted hydrogen	$\mathbf{As}'''H_3$.
Antimoniuretted hydrogen	$\mathbf{Sb}'''H_3$.
Solid phosphoretted hydrogen	$\mathbf{P}(P'''H)''$ / $\mathbf{P}(P'''H)''$.
Liquid „ „	$\mathbf{P}''_2H_4$.

GASEOUS PHOSPHORETTED HYDROGEN, $\mathbf{P}'''H_3$.

Molec. weight = 34. *Molec. vol.* □□. 1 *litre weighs* 17 *criths.* *Sp. gr.* 17.

Preparation. 1. It is evolved in a state of purity when either hypophosphorous or phosphorous acid is heated:

$$2\mathbf{P}^{v}OH_2Ho = \mathbf{P}^{v}OHo_3 + \mathbf{P}'''H_3.$$

Hypophosphorous acid. Phosphoric acid.

$$4\mathbf{P}^{v}OHHo_2 = 3\mathbf{P}^{v}OHo_3 + \mathbf{P}'''H_3.$$

Phosphorous acid. Phosphoric acid.

2. *Ordinary Method.* Heat fragments of phosphorus in a small vessel containing but little air with a strong solution of potassic or sodic hydrate:—

$$3\mathbf{O}KH + P_4 + 3\mathbf{O}H_2 = 3\mathbf{P}^{v}OH_2Ko + \mathbf{P}'''H_3.$$

Potassic hydrate. Potassic hypophosphite.

Properties. The gas produced by the latter method contains free hydrogen and vapour of liquid phosphoretted hydrogen ($'\mathbf{P}''_2H_4$), and is consequently spontaneously inflammable in air. When it is made to bubble up through water into still air, each bubble bursts into flame, and forms a graceful revolving wreath of white phosphoric acid. Brilliant flashes, attended by slight explosions, are produced if the bubbles are passed into a jar of oxygen.

$$\mathbf{P}H_3 + 2O_2 = \mathbf{P}^{v}OHo_3.$$

Mr. Graham discovered that small quantities of some inflammable vapours, such as ether, naphtha, &c., added to the gas, destroy this property. On the other hand the pure gas prepared by the first process does not take fire spon-

taneously, though the addition of $\frac{1}{10000}$ of its bulk of nitrous anhydride has the same effect upon it as the admixture of the vapour of liquid phosphoretted hydrogen. Gaseous phosphoretted hydrogen combines directly with nascent hydriodic and hydrobromic acids; the compounds formed are isomorphous with the corresponding substances in the nitrogen series ($\mathbf{N}^{v}H_4I$ and $\mathbf{N}^{v}H_4Br$), and are suggestive of the analogy between ammonia and phosphoretted hydrogen :—

$$3\mathbf{P}'''H_3 + 3HI = 3\mathbf{P}^{v}H_4I.$$

COMPOUNDS OF THE GROUP WITH CHLORINE.

Nitrous chloride—$\mathbf{N}'''Cl_3$?

Phosphorous, arsenious, antimonious, and bismuthous chlorides—$\mathbf{P}'''Cl_3$, $\mathbf{As}'''Cl_3$, $\mathbf{Sb}'''Cl_3$, and $\mathbf{Bi}'''Cl_3$.

Phosphoric and antimonic chlorides—$\mathbf{P}^{v}Cl_5$, $\mathbf{Sb}^{v}Cl_5$.

COMPOUNDS WITH OXYGEN AND HYDROXYL.

Nitrous oxide—$\mathbf{O}N'_2$.

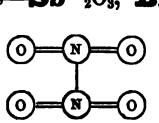
Nitric oxide—$\left\{\begin{matrix}\mathbf{N}O\\ \mathbf{N}O\end{matrix}\right.$ or $'\mathbf{N}''_2O_2$.

[Dibismuthous dioxide—$'\mathbf{Bi}''_2O_2$.]

Nitrous anhydride—$\mathbf{N}'''_2O_3$.

Phosphorous and arsenious anhydrides—$\mathbf{P}'''_2O_3$, $\mathbf{As}'''_2O_3$.

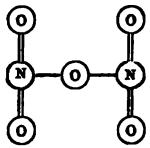
[Antimonious and bismuthous oxides—$\mathbf{Sb}'''_2O_3$, $\mathbf{Bi}'''_2O_3$.]

Nitric peroxide—$\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right.$ or $'\mathbf{N}^{iv}_2O_4$. 

[Diantimonic and dibismuthic tetroxides—

$'\mathbf{Sb}^{iv}_2O_4$ and $'\mathbf{Bi}^{iv}_2O_4$.]

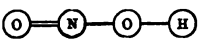
Nitric anhydride—$\left\{\begin{matrix}\mathbf{N}O_2\\O\\\mathbf{N}O_2\end{matrix}\right.$ or $\mathbf{N}^{v}_{2}O_5$.



Phosphoric, arsenic, antimonic, and bismuthic anhydrides—

$\mathbf{P}^{v}_{2}O_5$, &c.

Nitrous acid—$\mathbf{N}'''OHo$.



[Metantimonious and metabismuthous acids—

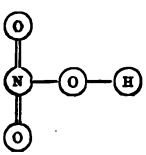
$\mathbf{Sb}'''OHo$ and $\mathbf{Bi}'''OHo$.]

Hypophosphorous acid—$\mathbf{P}^{v}OH_2Ho$.

Phosphorous and arsenious acids—

$\mathbf{P}^{v}OHHo_2$ and $\mathbf{As}^{v}OHHo_2$.

Nitric acid—$\mathbf{N}^{v}O_2Ho$.



Metaphosphoric, metantimonic, and metabismuthic acids (monobasic)—$\mathbf{P}^{v}O_2Ho$, &c.

Phosphoric, arsenic, and antimonic (?) acids (tribasic)—

$\mathbf{P}^{v}OHo_3$, &c.

Pyrophosphoric and pyrantimonic acids (tetrabasic)—

$\mathbf{P}^{v}_{2}O_3Ho_4$, &c.

? Hexabasic phosphoric acid—$\mathbf{P}^{v}_{4}O_7Ho_6$.

? Dodecabasic phosphoric acid—$\mathbf{P}^{v}_{10}O_{19}Ho_{12}$.

This group forms, with sulphur and hydrosulphyl, compounds which correspond to some of those in the foregoing table.

Of the oxides and acids of nitrogen it will be convenient to examine first nitric acid and nitric anhydride, chiefly because nitric acid and the nitrates play an important part in the preparation of the other members of the series.

NITRIC ACID, or *Hydric Nitrate*, NO_2Ho.

Molec. weight = 63. *Molec. vol.* □□. 1 *litre of vapour weighs* 31·5 *criths. Vap. sp. gr.* = 31·5. *Sp. gr.* 1·51. *Fuses at* − 50°. *Boils at* 84°·5.

The composition of this most important compound, formerly called *aquafortis*, was first ascertained by Cavendish, in 1785. Potassic nitrate, nitre, or saltpetre, a salt which occurs in tropical climates, especially in India, as an efflorescence on the soil, and sodic nitrate, which exists in large beds on the coasts of Chili and Peru, are examples of its combinations with the metals.

Preparation. 1. Some nitric acid is produced when a mixture of oxygen and nitrogen—atmospheric air, for example—is submitted to a succession of electric sparks in presence of moisture. It is thus formed in the atmosphere in small quantities by lightning. Traces of ammonic nitrate may almost invariably be detected in rain water.

2. This acid, or one of its salts, is also one of the products of the slow oxidation of organic matter containing nitrogen, in presence of powerful bases. The existence of nitrates in the well-water of towns is a certain indication that animal matters have been undergoing decomposition in the soil through which it has passed.

Manufacture.—Nitric acid is always prepared in chemical works and laboratories by distilling a mixture of sodic or potassic nitrate with concentrated sulphuric acid. If equal

weights of nitre and acid are employed, the following is the reaction:—

$$\underset{\text{Potassic nitrate.}}{\mathrm{N^{v}O_2Ko}} + \mathrm{S^{vi}O_2Ho_2} = \underset{\text{Hydric potassic sulphate.}}{\mathrm{S^{vi}O_2HoKo}} + \mathrm{N^{v}O_2Ho}.$$

On the large scale half this amount of sulphuric acid may be saved; but a higher temperature, which decomposes some of the nitric acid formed, is required; the following equations will explain the successive changes that take place:—

$$\underset{\text{Sodic nitrate.}}{2\mathrm{N^{v}O_2Nao}} + \mathrm{S^{vi}O_2Ho_2} = \underset{\text{Hydric sodic sulphate.}}{\mathrm{S^{vi}O_2HoNao}} + \underset{\text{Sodic nitrate.}}{\mathrm{N^{v}O_2Nao}}$$

$$+ \mathrm{N^{v}O_2Ho}.$$

$$\underset{\text{Hydric sodic sulphate.}}{\mathrm{S^{vi}O_2HoNao}} + \underset{\text{Sodic nitrate.}}{\mathrm{N^{v}O_2Nao}} = \underset{\text{Sodic sulphate.}}{\mathrm{S^{vi}O_2Nao_2}} + \mathrm{N^{v}O_2Ho}.$$

For the stoppered glass retort and cooled glass receiver employed in preparing nitric acid in the laboratory, the manufacturer substitutes a number of iron cylinders or retorts, arranged in a furnace, and connected by pipes with a series of large stoneware bottles.

Properties. The concentrated acid prepared in this way is —when not discoloured by the presence of much nitric peroxide—a quite colourless, or slightly yellowish, fuming, highly corrosive liquid (sp. gr. 1·51) which freezes at – 50°, and boils at 84°·5. Distillation (or even exposure to sunlight) occasions a partial decomposition of some of the acid, deepening its colour; the acid does not distil over unchanged at 84°·5, but oxygen and fumes of lower oxides of nitrogen are evolved, and the temperature slowly rises to about 121°, when a more stable but less concentrated acid having approximately the composition—$2\mathrm{N^{v}O_2Ho,3OH_2}$—distils over.

Nitric acid is monobasic and produces nitrates, nearly all

of which are soluble in water, by its action on metallic oxides or hydrates, *e.g.*—

$$\underset{\text{Potassic hydrate.}}{\mathbf{O}KH} + \mathbf{N}^{v}O_2Ho = \underset{\text{Potassic nitrate.}}{\mathbf{N}^{v}O_2Ko} + \mathbf{O}H_2.$$

$$\underset{\text{Plumbic oxide.}}{\mathbf{Pb}''O} + 2\mathbf{N}^{v}O_2Ho = \underset{\text{Plumbic nitrate.}}{\left\{\begin{matrix}\mathbf{N}O_2\\ Pbo''\\ \mathbf{N}O_2\end{matrix}\right.} + \mathbf{O}H_2.$$

The action of metals upon this acid differs considerably from their behaviour with sulphuric acid, a compound of far greater stability. Zinc, for instance, simply displaces the hydrogen of sulphuric acid, forming zincic sulphate (see pp. 39, 65); but, with *cold* nitric acid, zinc, and copper or mercury, silver, and tin yield respectively nitrous and nitric oxides, nitrous anhydride, and nitric peroxide, under the circumstances, and in the manner indicated in the description of the processes for preparing these several compounds (v. infra)—reactions bearing a resemblance to the behaviour of sulphuric acid when *boiled* with some metals such as copper, mercury, arsenic, tin, lead, silver, &c., but differing in one important respect, viz., that no elevation of temperature is needed to assist the decomposition. With highly concentrated nitric acid copper acts in the same manner as tin, whilst with the aid of heat it may be made to liberate free nitrogen. Zinc or tin with strong acid produces some ammonia which combines with the excess of acid:—

$$Zn_4 + \underset{\text{Nitric acid.}}{10\mathbf{N}^{v}O_2Ho} = \underset{\text{Zincic nitrate.}}{4\mathbf{N}^{v}_2O_4Zno''} + \underset{\text{Ammonic nitrate.}}{\mathbf{N}^{v}O_2(N^{v}H_4O)} + 3\mathbf{O}H_2.$$

All the metals, except gold and platinum and two or three still rarer elements, are attacked by nitric acid, especially when it is diluted to a specific gravity of 1·35 to 1·25. It gives up part of its oxygen to all the non-metals except chlorine,

bromine, nitrogen, and oxygen itself; hot powdered charcoal, for instance, treated with a drop or two of nitric acid burns brightly. Owing to the ease with which this acid parts with a portion of the 76 per cent. of oxygen that it contains, it is perhaps the best oxidising agent in use. Nitrous acid, on account of its greater instability, adds considerably by its presence to the oxidising power of nitric acid. Animal textures are quickly destroyed by the action of the strong acid; when more dilute it stains skin, wool, &c., of a bright yellow. It oxidises and destroys the colour of indigo. No definite hydrates of the acid are known to exist. *Aqua regia* and nitro-muriatic acid are the names given to a mixture of nitric with hydrochloric acid: such a mixture has the power of dissolving platinum and gold and other substances on which neither acid alone has any action. The commercial acid is apt to be contaminated with some sulphuric acid and chlorine (detected by means of baric sulphate and argentic nitrate respectively) and some potash and ferric oxide.

Tests. (See note p. 51.) 1. Dilute nitric acid with a few copper clippings gives off red fumes of nitric peroxide.

2. Add to a small quantity of the solution of a nitrate or of nitric acid a crystal—or a few drops of a concentrated solution—of ferrous sulphate, and then pour in gradually a little strong sulphuric acid: between the heavy acid and the liquid above it a brown coloration appears.

Uses. For etching on copper, and as a solvent for metals, as well as in the manufacture of gun-cotton, nitro-benzol, &c., this acid is employed. A very dilute solution is used for giving a yellow dye to woollen and silken fabrics. It is the most important agent chemists possess for oxidising purposes.

NITRIC ANHYDRIDE, N_2O_5.

Probable molec. weight = 108. *Probable molec. vol.* □□.
Fuses at 29°·5. *Boils at* 45°.

Preparation. Pass dry chlorine over crystals of carefully

dried argentic nitrate heated to about 95°, and condense the anhydride in a receiver surrounded by a freezing mixture.

$$\underset{\text{Argentic nitrate.}}{4N^{v}O_2Ago} + 2Cl_2 = \underset{\text{Argentic chloride.}}{4AgCl} + \underset{\text{Nitric anhydride.}}{2N^{v}_2O_5} + O_2.$$

Properties. The transparent, white crystalline substance obtained is of a very unstable character, and breaks up even at the ordinary temperature, sometimes bursting the sealed tubes in which the crystals have been preserved. It dissolves in water with the extrication of much heat.

$$N^{v}_2O_5 + OH_2 = 2N^{v}O_2Ho.$$

NITROUS OXIDE, ON'_2.

Molec. weight = 44. *Molec. vol.* □□. 1 *litre weighs* 22 *criths.*
Sp. gr. 22. *Fuses at* − 101°. *Boils at* − 88°.

Preparation. Heat ammonic nitrate in a flask or retort; the salt melts and breaks up into steam and nitrous oxide or *laughing gas*, which should be collected over warm water.

$$\underset{\text{Ammonic nitrate.}}{N^{v}O_2(N^{v}H_4O)} = 2OH_2 + \underset{\text{Nitrous oxide.}}{ON'_2}.$$

Properties. This gas is transparent and colourless, and has a faint sweet taste. Its specific gravity is the same as that of carbonic anhydride, viz. 22. The tension of nitrous oxide at 0° is 30 atmospheres, and at − 88° one atmosphere: in other words, it liquefies under a pressure of 30 atmospheres at 0°, or at − 88° under the normal atmospheric pressure; the colourless liquid into which it is converted freezes and forms a transparent crystalline solid at about − 101°. When evaporated *in vacuo* with carbonic disulphide, liquid nitrous oxide produces the greatest depression of temperature ever yet attained—a temperature so low, in fact, that it renders even alcohol viscid and is calculated to be not less than 140° C

below the freezing point of water. One volume of water dissolves at 15° about 0·77—or at 0° 1·305—volumes of this gas; in warm water it is less soluble.

The name "laughing gas" has been given to this compound on account of the intoxicating effect—often accompanied by a tendency to violent laughter—which it produces when inhaled for a few moments. A glowing match rekindles on being plunged into the gas, and many substances, phosphorus for instance, burn in nitrous oxide with a brilliancy second only to that attending their combustion in oxygen. These properties are due to the ease with which the gas breaks up into its constituents—as when it is passed repeatedly through a red-hot porcelain tube—forming a mixture of nitrogen with a larger proportion of oxygen than that existing in atmospheric air. Comparative insolubility in water, and the property of producing red fumes with nitric oxide, distinguish oxygen from nitrous oxide—whose composition may be accurately ascertained either by a eudiometric process similar to that pursued in the case of atmospheric air (p. 120), or by heating, with certain precautions, in a measured volume of the gas a piece of potassium till it burns, leaving a volume of nitrogen equal to that originally occupied by the nitrous oxide:—

$$\mathbf{O}N'_2 + K_2 = \mathbf{O}K_2 + N_2.$$

Nitrous oxide cannot be regarded either as an anhydride or a base.

NITRIC OXIDE, $'\mathbf{N}''_2O_2$.

Molec. weight = 60. *Molec. vol. anomalous** . 1 *litre weighs* 15 *criths. Sp. gr.* 15.

Preparation. Dilute nitric acid (sp. gr. 1·2) poured on copper clippings or mercury acts in the following manner:—

* V. infra, p. 196.

$$8\underset{\text{Nitric acid.}}{N^{V}O_2H} + 3Cu = 3\underset{\text{Cupric nitrate.}}{N^{V}_2O_4Cuo''} + \underset{\text{Nitric oxide.}}{N''_2O_2} + 4OH_2.$$

Properties. Nitric oxide is a transparent, colourless gas, which has never been liquefied, and of which water dissolves but $\frac{1}{20}$th of its volume.

Contact with air or oxygen converts nitric oxide into red suffocating fumes of nitrous anhydride and nitric peroxide; these are soluble in water. Nitric oxide is hence used as a test to detect the presence of free oxygen in a gaseous mixture. In the manufacture of sulphuric acid we have seen that it plays the important part of a carrier of oxygen. This gas is a stable compound and refuses to decompose except at a high temperature; hence it extinguishes the combustion of some bodies, such as a lighted taper, whilst phosphorus, charcoal, &c., when burning vigorously, deflagrate with brilliancy on introduction into this gas. A mixture of nitric oxide with vapour of carbonic disulphide gives on ignition a very bright flash of light so rich in chemical rays that it effects the explosion of a mixture of hydrogen and chlorine in the same manner as direct sunlight. Nitric oxide is absorbed by a solution of ferrous sulphate and produces a reddish-brown liquid, which absorbs oxygen rapidly from the air. Nitric acid, unless very dilute, absorbs the gas, and if concentrated becomes reddish-brown. Nitric oxide is neither a base nor an anhydride.

NITROUS ANHYDRIDE, N'''_2O_3.

Molec. weight = 76. *Molec. vol.* $\square\square$.

Preparation. 1. Mix four volumes of dry nitric oxide with one volume of oxygen; brownish-red fumes of nitrous anhydride, which at — 18° are condensed into a blue liquid, are formed.

2. Heat nitric acid (sp. gr. 1·25) with starch.

3. Dissolve silver in cold dilute nitric acid: nitrous acid remains in solution:—

$$\underset{\text{Nitric acid.}}{6\mathbf{N}^{v}O_2Ho} + 2Ag_2 = \underset{\text{Argentic nitrate.}}{4\mathbf{N}^{v}O_2Ago} + 3\mathbf{O}H_2 + \mathbf{N}'''_2O_3.$$

Properties. Nitrous anhydride is a blue, volatile, unstable liquid which boils at about 0° forming red vapours; it is decomposed into nitric acid and nitric oxide by much water; a little water converts it into nitrous acid.

NITROUS ACID, *Hydric Nitrite*, $\mathbf{N}'''OHo$.

Molec. weight = 47.

Properties. This acid acts both as a reducing and as an oxidising agent: in its reducing capacity it becomes converted into nitric acid at the expense of dipotassic permanganate, $\left\{\begin{matrix}'\mathbf{Mn}^{v}O_2—O—Ko \\ '\mathbf{Mn}^{v}O_2—O—Ko'\end{matrix}\right.$ and destroys the violet colour of the solution. Nitrous acid is monobasic, and forms with metallic oxides or hydrates a class of salts named nitrites:—

$$\underset{\text{Nitrous acid.}}{\mathbf{N}'''OHo} + \mathbf{O}KH = \underset{\text{Potassic nitrate.}}{\mathbf{N}'''OKo} + \mathbf{O}H_2.$$

Potassic nitrite may be obtained by heating potassic nitrate, or nitre, to redness. Nitrites, like nitrates, are found in water which has passed over decomposing animal matter; oxidation converts them into nitrates.

NITRIC PEROXIDE, $'\mathbf{N}^{iv}{}_2O_4$.

Molec. weight 92. *Molec. vol. below* 0° , *at* 100°

Preparation. 1. Pass nitric oxide and oxygen—which, as

we have seen, combine together directly—into some perfectly dry tubes cooled by a mixture of ice and salt:—

$$'N''_2O_2 + O_2 = 'N^{iv}_2O_4.$$

2. Plumbic nitrate heated in a hard glass retort yields a mixture of oxygen and nitric peroxide:—

$$2N^{v}_2O_4Pbo'' = 2Pb''O + 2N_2O_4 + O_2.$$

3. Under certain circumstances tin may be made to act on nitric acid in the following manner:—

$$\underset{\text{Nitric acid.}}{20NO_2Ho} + Sn_5 = \underset{\text{Metastannic acid.}}{Sn^{iv}_5O_5Ho_{10}} + 5OH_2 + 10N_2O_4.$$

Properties. Nitric peroxide is obtained by the first process in the form of yellow prismatic crystals; these produce, on melting at about — 12° (Müller), a yellow, volatile liquid, which reddens as the temperature rises, and boils at 22°. A small trace of water suffices to decompose it and to convert it into a yellow, green, or blue liquid; nitric acid is thus formed and nitric oxide liberated: $3N_2O_4 + 2OH_2 = 4NO_2Ho + N_2O_2$. Nitric peroxide vapour is deep brownish-red in colour—at 100° almost opaque—and has a suffocating odour; its specific gravity, if the formula $'N^{iv}_2O_4$ represents its structure accurately, should be 46—in order to accord with Ampère's law; but from a low temperature upwards the expansion of this vapour, for every degree of rise, is abnormally great, so that at 100° nitric peroxide occupies nearly double its normal volume: many chemists have on this account assigned NO_2 as the correct formula for the molecule,—whilst to others it seems unnecessary to adopt this view, and thus to create an exception to important laws otherwise apparently absolute (pp. 61—63). The anomaly in the molecular volume of nitric oxide noticed above (p. 193), does not demand that the formula $'N''_2O_2$ should be halved. Till more light has been

thrown upon this question, the theory that whatever dissociation or change in physical structure has taken place in nitric peroxide vapour at 100° takes place in the case of nitric oxide at a lower temperature—is at least allowable.

Nitric peroxide vapour supports several forms of combustion, and causes potassium to ignite spontaneously. This compound has no acid or basic properties; with metallic hydrates or oxides it produces a mixture of nitrates and nitrites:—

$$2\mathbf{O}KH + \mathbf{N}^{IV}_2O_4 = \mathbf{N}^{V}O_2Ko + \mathbf{N}'''OKo + \mathbf{O}H_2.$$

Potassic hydrate. Potassic nitrate. Potassic nitrite.

PHOSPHOROUS ANHYDRIDE, $\mathbf{P}'''_2O_3$.

Molec. weight = 110.

Preparation. Let phosphorus either burn or slowly oxidise in a limited current of dry air.

Properties. A white, volatile, deliquescent, inflammable powder without crystalline structure may be thus obtained; it combines energetically with water, producing phosphorous acid.

PHOSPHOROUS ACID, $\mathbf{P}^{V}OHHo_2$.

Molec. weight = 82.

Preparation. 1. $\mathbf{P}'''_2O_3 + 3\mathbf{O}H_2 = 2\mathbf{P}^{V}OHHo_2$.

2. Phosphorus oxidises slowly in moist air and forms this acid.

3. Water and phosphorous trichloride—the product of the action of chlorine on phosphorous—yield hydrochloric and phosphorous acids:—

$$\mathbf{P}'''Cl_3 + 3\mathbf{O}H_2 = 3HCl + \mathbf{P}^{V}OHHo_2.$$

Properties. If phosphorous acid be prepared by the third method, and freed from hydrochloric acid by a heat not ex-

ceeding 200°, it may be procured in deliquescent crystals which absorb oxygen on exposure to the air:

$$\underset{\text{Phosphorous acid.}}{2\mathbf{P}^{v}0HHo_2} + O_2 = \underset{\text{Phosphoric acid.}}{2\mathbf{P}^{v}0Ho_3}.$$

A high temperature has the following effect on phosphorous acid:

$$\underset{\text{Phosphorous acid.}}{4\mathbf{P}^{v}0HHo_2} = \underset{\text{Phosphoric acid.}}{3\mathbf{P}^{v}0Ho_3} + \underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}'''H_3}.$$

This acid is dibasic: sodic phosphite, $\mathbf{P}^{v}0HNao_2$, and dihydric baric phosphite, $\mathbf{P}^{v}_2O_2H_2Ho_2Bao''$, are representatives of its two classes of salts.

PHOSPHORIC ANHYDRIDE, $\mathbf{P}^{v}_2O_5$.

Molec. weight = 142.

Preparation. Burn successive fragments of phosphorus in the centre of a large three-necked glass globe, through which a continuous current of dry air is made to pass.

Properties. A snow-white, non-crystalline, highly deliquescent powder is thus obtained. At high temperatures it is volatile, and may be sublimed. Its great avidity for moisture renders it useful as the best desiccator of many gases. It unites with water with a hissing noise, forming metaphosphoric acid:—

$$\underset{\text{Phosphoric anhydride.}}{\mathbf{P}^{v}_2O_5} + OH_2 = \underset{\text{Metaphosphoric acid.}}{2\mathbf{P}^{v}O_2Ho}.$$

METAPHOSPHORIC ACID, $\mathbf{P}^{v}O_2Ho$.

Molec. weight = 80.

Preparation. 1. Treat the anhydride with water (v. supra).

2. Heat phosphoric acid to redness:—

$$\underset{\text{Phosphoric acid.}}{\mathbf{P}^{v}OHo_3} = \underset{\text{Metaphosphoric acid.}}{\mathbf{P}^{v}O_2Ho} + \mathbf{O}H_2.$$

Properties. When boiled, the aqueous solution of this monobasic acid is converted—by the reversion of the above action—into the ordinary tribasic acid. The metaphosphates may be prepared by several processes, *e.g.*,

1. By igniting a dihydric phosphate which has a fixed base:—

$$\underset{\text{Dihydric sodic phosphate.}}{\mathbf{P}^{v}OHo_2Nao} = \underset{\text{Sodic metaphosphate.}}{\mathbf{P}^{v}O_2Nao} + \mathbf{O}H_2.$$

2. By igniting a monohydric phosphate containing one atom of a volatile base, *e.g.*, "microcosmic salt:"—

$$\underset{\text{Hydric sodic ammonic phosphate.}}{\mathbf{P}^{v}OHoNao(N^{v}H_4O)} = \underset{\text{Sodic Metaphosphate.}}{\mathbf{P}^{v}O_2Nao} + \underset{\text{Ammonia.}}{\mathbf{N}^{v}H_4Ho}.$$

PYROPHOSPHORIC ACID, $\mathbf{P}^{v}{}_2O_3Ho_4$.

Molec. weight = 178.

Preparation. Plumbic pyrophosphate, precipitated by sodic pyrophosphate from a solution of plumbic acetate, is suspended in water, and decomposed by means of sulphuretted hydrogen:—

$$\underset{\text{Plumbic pyrophosphate.}}{\mathbf{P}^{v}{}_2O_3Pbo''_2} + 2\mathbf{S}''H_2 = \underset{\text{Plumbic sulphide.}}{2\mathbf{Pb}''S} + \underset{\text{Pyrophosphoric acid.}}{\mathbf{P}^{v}{}_2O_3Ho_4}.$$

Properties. This solution yields, on evaporation *in vacuo*, over sulphuric acid, crystals of tetrabasic phosphoric acid, or pyrophosphoric acid (πῦρ, fire), so called because the pyrophosphates are prepared by heating to redness such tribasic phosphates as are monohydric and contain two atoms of a fixed base:—

$$\underset{\text{Hydric disodic phosphate.}}{2\mathbf{P}^{v}OHoNao_2} = \underset{\text{Sodic pyrophosphate.}}{\mathbf{P}^{v}{}_2O_3Nao_4} + \mathbf{O}H_2.$$

PHOSPHORIC ACID, *Orthophosphoric Acid, Trihydric Phosphate,* $\mathbf{P^{v}}OHo_3$.

Molec. weight = 98.

Preparation. 1. Boil the aqueous solution of phosphoric anhydride or of metaphosphoric acid:—

$$\mathbf{P^{v}}_2O_5 + 3\mathbf{O}H_2 = 2\mathbf{P^{v}}OHo_3.$$

2. Oxidise amorphous phosphorus by heating it with nitric acid (sp. gr. 1·2) which becomes reduced to the lower gaseous oxides of nitrogen.

3. Evaporate tricalcic diphosphate (bone-ash) with a large excess of sulphuric acid; tetrahydric calcic sulphate (gypsum) crystallises out; on adding to the residual solution ammonic carbonate, till effervescence ceases, filtering, evaporating to dryness the solution obtained, and igniting the residue, phosphoric acid is separated:—

$$\underset{\text{Tricalcic diphosphate.}}{\mathbf{P^{v}}_2O_2Cao''_3} + 3\underset{\text{Sulphuric acid.}}{\mathbf{S^{vi}}O_2Ho_2} + 6\mathbf{O}H_2 = 2\underset{\text{Phosphoric acid.}}{\mathbf{P^{v}}OHo_3} + 3\underset{\text{Tetrahydric calcic sulphate.}}{\mathbf{S^{vi}}Ho_4Cao''}.$$

Properties. When the colourless liquid prepared by the second process is boiled, and then allowed to cool, the acid forms a transparent, glassy, very deliquescent solid; this is called *glacial phosphoric acid.* The concentrated solution of this substance is intensely acid, and has the sp. gr. 2; a temperature of 213° converts it into pyrophosphoric acid:—

$$2\mathbf{P^{v}}OHo_3 = \mathbf{P^{v}}_2O_3Ho_4 + \mathbf{O}H_2.$$

The following phosphates of sodium, &c., are examples of the important class of salts formed by this acid:—

Dihydric sodic phosphate ..... $\mathbf{P}^{v}0Ho_2Nao.$
Hydric disodic phosphate (*common rhombic sodic phosphate*) ..... $\mathbf{P}^{v}0HoNa_2.$
Hydric sodic potassic phosphate ..... $\mathbf{P}^{v}0HoNaKo.$
Trisodic phosphate..... $\mathbf{P}^{v}0Na_3.$

Tests. With a solution of argentic nitrate these salts give a canary-yellow precipitate of triargentic phosphate:—

$$\underset{\text{Hydric disodic phosphate.}}{\mathbf{P}^{v}0HoNa_2} + \underset{\text{Argentic nitrate.}}{3\mathbf{N}^{v}0_2Ago} = \underset{\text{Sodic nitrate.}}{2\mathbf{N}^{v}0_2Nao} + \underset{\text{Nitric acid.}}{\mathbf{N}^{v}0_2Ho} + \underset{\text{Triargentic phosphate.}}{\mathbf{P}^{v}0Ago_3}:$$

Sodic pyrophosphate, on the other hand, gives a white precipitate of argentic pyrophosphate:—

$$\underset{\text{Sodic pyrophosphate.}}{\mathbf{P}^{v}_20_3Nao_4} + 4\mathbf{N}^{v}0_2Ago = 4\mathbf{N}^{v}0_2Nao + \underset{\text{Argentic pyrophosphate.}}{\mathbf{P}^{v}_20_3Ago_4}:$$

whilst sodic metaphosphate produces a white gelatinous precipitate of argentic metaphosphate, soluble in excess of sodic metaphosphate.

$$\underset{\text{Sodic metaphosphate.}}{\mathbf{P}^{v}0_2Nao} + \mathbf{N}^{v}0_2Ago = \mathbf{N}^{v}0_2Nao + \underset{\text{Argentic metaphosphate.}}{\mathbf{P}^{v}0_2Ago}.$$

Metaphosphoric acid may also be distinguished from pyrophosphoric and tribasic phosphoric acids by the property which it possesses of coagulating albumen.

COMPOUND OF NITROGEN WITH CARBON.

Cyanogen ..... $\left\{\begin{matrix}\mathbf{C}\mathbf{N}'''\\ \mathbf{C}\mathbf{N}'''.\end{matrix}\right.$

The study of this very important gas and compound radical belongs rather to organic than to inorganic chemistry.

GLOSSARY.

Abnormal, (*ab*, out of,—*norma*, a square), not normal, irregular.

Aggregation, state of, (*aggregatus*, joined together), the condition in which the parts of a mass are collected together.

Amorphous (*a*, without,—*μορφή*, form, shape), of irregular shape, not crystalline.

Barometer, (*βάρος*, weight,—*μέτρον*, a measure), an instrument for measuring the weight or pressure of the atmosphere.

Calcination, (*calx*, lime), the operation of heating a substance so as to expel volatile matters and reduce it to a friable state.

Calorimeter, (*calor*, heat,—*μέτρον*), an instrument to measure relative quantities of heat, or to determine specific heats.

Capillarity, (*capillus*, a hair), resemblance to a hair, fineness, smallness in diameter.

Catalysis, (*κατάλυσις*,—*κατά*, down,—*λύσις*, a loosing), a chemical action in which a substance induces decomposition in another body, without itself entering into combination.

Desiccate, (*desiccare*, to dry up), to dry ; to remove moisture from.

Formula, (Lat. *formula*), a mode of expression.

Hygrometer, (*ὑγρόν*, moisture,—*μέτρον*), an instrument for measuring the moisture of the atmosphere.

Hopothesis, (*ὑπόθεσις*,—*ὑπό*, under,—*θέσις*, a placing), a supposition ; a proposition assumed in order to account for phenomena.

Nascent, (*nascens*, being born, beginning), becoming free, in the act of being liberated (applied to a gas).

Nomenclature, (*nomenclatura*,—*nomen*, a name,—*calo*, I call), a system or vocabulary of names appropriated to any particular branch of science.

Normal, (*norma*, a rule), according to rule, regular, usual.

Sublimation, (*sublimare*, to elevate), the operation of converting a solid into vapour by heat and condensing it again as a solid.

Symbol, (*σύμβολον*), a sign of any thing or idea.

Theory, (*θεωρέω*, to look at, contemplate, speculate upon), speculation, a doctrine founded on established principles and giving a philosophical explanation of phenomena.

Thermic, and thermal, (*θερμόν*, heat), of or pertaining to heat.

Vacuum, (*vacuus*, empty), space empty or devoid of all matter.

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